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Pressure effects of optically transparent gases on molecular Rydberg transitions

Judith L. Adolph

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Pressure Effects of Optically Transparent Gases
On Molecular Rydberg Transitions

By
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B.A., University of California at Santa Barbara, 1978

Presented in partial fulfillment of the requirements
for the degree of Master of Science

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A model is developed to permit calculation of excited-state intermolecular Van der Waals forces from the broadening and shift of absorption spectra at different pressures of a non-absorbing gas. The non-absorbing or optically transparent gas is termed the perturber while the molecule which interacts with the light radiation is termed the absorber. Perturber gas pressures ranged from 0 to 25 bar. The study is confined to absorber Rydberg states because of their susceptibility to perturbation.

A Lennard-Jones 6,12 potential is used to define the intermolecular forces between the absorber and perturber. The potential is related to absorbance by coefficients, $C_i$, which are determined from the following expansion:

$$A^p(\tilde{v}) = \tilde{v} \sum_{i=0}^{\infty} C_i \frac{d}{d\tilde{v}} \left[ \frac{A^o(\tilde{v})}{\tilde{v}} \right]$$

$A^p(\tilde{v})$ and $A^o(\tilde{v})$ are the experimental absorption spectra with and without perturbation, respectively. The theoretical form of the coefficients, as developed in this paper, allows calculation of the Lennard-Jones parameters from the experimentally measured $C_i$ values. The consistency and validity of the model in terms of the physical forces it is attempting to predict are discussed in detail.

Systems investigated include CH$_3$I with SF$_6$ and thiirane with SF$_6$. A and CF$_4$. Thiirane is shown to be affected more by the applied perturbation than CH$_3$I. In addition, the Lennard-Jones potential-well depth exhibits a far greater percent change between the ground and excited states than does the intermolecular distance, which remains almost unchanged. Lastly, the change of the potential-well depth in the excited state is shown to correlate well with the appearance of satellite bands which are present for pressures greater than 4 bar.
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Introduction

The broadening and shift of spectral lines, first treated by Lorenz in 1906, has been a subject of increasing interest since the 1930's. Numerous techniques and interaction potentials have been utilized to explain these effects with varying degrees of success. This paper considers only the Lennard-Jones 6,12 potential. The spectral series analyzed occur in the vacuum ultraviolet region, 2000-1300 Å. In addition, emphasis was given to Rydberg states as the effect on these states by an outside pressure perturbation is quite dramatic.

In ideal cases Rydberg transitions of molecules may be recognized by their frequencies, ν, which fit the series

\[ hν = \sigma_i - \frac{R}{(n - \delta)^2} \]

where \( \sigma_i \) is the ionization potential, R is the Rydberg constant \((1.09737 \times 10^{-5} \text{ cm}^{-1})\) and \( \delta \) is termed the quantum defect \((1)\). Theoretically the transitions are characteristic of a one electron system in which the optical electron is at so large a distance from the core that the core appears as a point charge. The quantum-defect term reflects the deviation of the core from a point charge. The optical electron is in an orbital with a very large relative radius; therefore, it is quite sensitive to perturber gas pressures. Valence-shell transitions are much less sensitive to external perturbations \((1)\). Thus, the application of pressure serves as a device to identify Rydberg transitions, even if there is difficulty in fitting them to the Rydberg equation. Figure 1 shows the extensive broadening of a methyl iodide Rydberg band when
pressurized with nitrogen. In contrast, the valence shell transition of benzene shows almost no change when pressurized with 136 atm of helium.

The technique of utilizing a potential curve for band analysis is illustrated in Figure 2. Curve I shows both molecules in the ground state. There is a van der Waals attraction at large intermolecular distances; however, as the molecules are brought closer together the charge clouds overlap and the interaction quickly becomes repulsive. Curve II represents the absorber in a Rydberg excited state which, due to some property of the perturber, such as electron affinity, is stabilized and therefore shifted to lower energy. The last potential curve (curve III) represents the destabilization of the absorber Rydberg state by the perturber. Here the large size of the Rydberg orbital and the resulting repulsive forces dominate.

In order to determine numerical values for the molecular interaction parameters in the Rydberg state, the Lennard-Jones potential was used in the development of a theoretical model. The utilization of this model required a Taylor expansion (24) where the absorption spectrum with perturbation applied, $A^p(\tilde{v})$, is expressed in terms of the absorption spectrum without perturbation, $A^o(\tilde{v})$;

$$A^p(\tilde{v}) = \tilde{v} \sum_{i=0} C_i \frac{d^i[A^o(\tilde{v})/\tilde{v}]}{d\tilde{v}}$$  \hspace{1cm} (1)

(For derivation of this equation see Appendix A.)

Using a moment analysis the above equation is solved to yield a set of coefficients, $C_i$. These coefficients include information regarding the excited state van der Waals constants.
Figure 1. The $^1A_{1g} \rightarrow ^1B_{2n}$ transition of benzene before and after the addition of 136 atm of helium gas shows the lack of broadening characteristic of valence shell transitions. This contrasts with the extensive asymmetric broadening of the $5p \rightarrow 6s$ Rydberg transition of methyl iodide. From "Higher Excited States of Polyatomic Molecules," Vol. 1, Melvin B. Robin.
Figure 2. Potential energy curves representing the interaction of an absorber-perturber pair. Curve I depicts both molecules in the ground state. Curves II and III show stabilization and destabilization of the Rydberg state, respectively.
Theory

The theoretical aspect of this work consisted of deriving molecular interaction potentials from the broadening and shift of a spectral band. The broadening and shift of the band resulted from increasing pressures of a non-absorbing gas. In the development of this model several approximations, assumptions and definitions were made.

The first approximation attributes any shift in a spectrum to a change only in energy, while the wavefunction remains unperturbed. Perturbation theory of non-degenerate states tells us that to a first-order approximation the perturbation energy can be expressed as

$$E^{(1)} = <\psi^{(0)} | H^{(1)} | \psi^{(0)} >$$

where the perturbation is averaged over the wavefunction of the unperturbed state. While it would certainly be necessary to include higher order approximation equations at greater pressures, it will be shown that the wavefunction perturbation is quite small for pressures less than 5 bar; therefore the first-order energy equation is sufficient.

The coefficients, $C_i$, in Eq. (1) are expressed as

$$C_i = (-1)^{i-1} \frac{i!}{i!} \frac{\int r \Omega(r) D^i(r) \Gamma(r) dr}{\int \Omega(r) dr}$$

where $\Omega(r)$ represents the molecular distribution, $D^i(r)$ the energy shift of the absorption band and $\Gamma(r)$ the transition probability of the perturbed system relative to the transition probability of the unperturbed system. The only coordinate considered is the intermolecular separation.
These quantities will be defined specifically for this model later in this section. If no wavefunction perturbation exists, $\Gamma(r) = 1$ and the expression simplifies to

$$C_1 = \frac{(-1)^i}{i!} \frac{\int_{\mathbb{R}} \Omega(r) \frac{d}{dr} \Omega(r) \, dr}{\int_{\mathbb{R}} \Omega(r) \, dr}.$$  \hspace{1cm} (4)

Therefore, we are concerned only with an energy shift which is a function of the absorber-perturber coordinate, and with the molecular distribution. (Appendix B discusses $\Gamma \neq 1$).

The last approximation deals with absorber-perturber relationships. The model considers only absorber-perturber pairs. Again, the only coordinate is the intermolecular separation. This simplifies calculations considerably but introduces increasing error as a molecule deviates from spherical symmetry.

The basic assumption of the model is the use of the Lennard-Jones potential

$$U(r) = 4\varepsilon \left( \sigma^{12}/r^{12} - \sigma^6/r^6 \right). \hspace{1cm} (5)$$

Specifically, for this model the potentials of the ground state and excited state are expressed respectively as

$$U(r) = 2D_e \left( r_e^{12}/2r^{12} - r_e^6/r^6 \right) \hspace{1cm} (6)$$

and

$$U'(r) = 2D'_e \left( r_e^{12}/2r^{12} - r_e^6/r^6 \right). \hspace{1cm} (7)$$
The following customary equations and relationships were used:

\[ \varepsilon_{12} = (\varepsilon_{11} \varepsilon_{22})^{1/2}, \quad (8) \]

\[ \sigma_{12} = \frac{1}{2}(\sigma_{11} + \sigma_{22}), \quad (9) \]

\[ 2^{1/6} \sigma = r_e, \text{ where } r_e \text{ is the position of the potential minimum}, \quad (10) \]

and

\[ D_e = \varepsilon, \text{ the potential well depth}. \quad (11) \]

The energy shift of the band can now be expressed as

\[ D(r) = U'(r) - U(r). \quad (12) \]

The volume occupied by the perturber molecules is assumed to be that of an ideal gas

\[ V = kT/P. \]

Furthermore it is assumed that each volume is a sphere of radius

\[ R = \left( \frac{3kT}{4\pi P} \right)^{1/3}, \quad (13) \]

where \( R \) is used as the upper integration limit in Eq. 4.

The model utilizes a Boltzmann distribution for the ground state absorber-perturber intermolecular distance. A continuous energy distribution for both the ground and excited states is also assumed.

The following quantity is defined:

\[ D_p^n \equiv \frac{\int_0^R [D(r)]^n \exp \left[-U(r)/kT\right]r^2dr}{\int_0^R \exp \left[-U(r)/kT\right]r^2dr}. \quad (14) \]

Coefficients are now readily expressed as

\[ C_i = (-1)^i D_p^i/i!. \quad (15) \]
The correlation between the experimental coefficients and the desired intermolecular parameters \((r_e, r'_e, D_e\) and \(D'_e)\) can now be made.

For this model, knowledge of the first three coefficients was adequate to determine the intermolecular parameters. These are

\[
C_0 = (-1)^0 D_p^0 / 0! = 1
\]  \hspace{1cm} (16)

\[
C_1 = (-1)^1 D_p^1 / 1! = -\left\{ 2[D_e - D_e' r_e^6 / r_e^6] F_{-1}(b, r_e / R) - \right. \\
\left. [D_e - D_e' r_e^{12} / r_e^{12}] F_1(b, r_e / R) / F_{-3}(b, r_e / R) \right\},
\]  \hspace{1cm} (17)

\[
C_2 = (-1)^2 D_p^2 / 2! = \left\{ 2[D_e - D_e' r_e^6 / r_e^6]^2 F_1(b, r_e / R) - \right. \\
\left. 2[D_e - D_e' r_e^6 / r_e^6] \times [D_e - D_e' r_e^{12} / r_e^{12}] F_3(b, r_e / R) \right. \\
\left. + \frac{3}{2}[D_e - D_e' r_e^{12} / r_e^{12}]^2 F_5(b, r_e / R) / F_{-3}(b, r_e / R) \right\}
\]  \hspace{1cm} (18)

where

\[
b \equiv D_e / kT,
\]

and

\[
F_n(b, r_e / R) \equiv \int_0^\infty \exp \left[ -b(x-1)^2 \right] x^n / 2 \, dx.
\]  \hspace{1cm} (19)

(For explicit derivations see Appendix C.)

This set of approximations, assumptions and equations represents the theoretical model. Experimentally determined coefficients analyzed in this context allowed the intermolecular parameters to be estimated.

The calculation of intermolecular parameters from the broadening and shift of spectral bands via a simplistic form of a chemical potential has been gaining in popularity since 1970. The square well potential has been shown to predict correctly the direction of energy shift.
and appearance of satellites in spectra (5, 8 and 16) when a pressure perturbation is applied. Robin and Kuebler (9) proposed using the Lennard-Jones 6,12 potential to explain the changes with pressure exhibited in spectra, however had little success in calculating numerical values for the intermolecular parameters. Since then, several authors (4, 17, 18, 19 and 26) have used the Lennard-Jones potential to calculate numerical values for these parameters. However, the problem was treated in a time dependent framework. The calculation of intermolecular parameters by a time independent method greatly simplifies calculations and is believed to be unique to this work.
Materials and Methods

The spectra of methyl iodide perturbed with sulfur hexafluoride were taken on a McPherson Model-240, 2 meter vacuum monochromator equipped with a 1200 line/mm grating. First-order reciprocal dispersion of this grating was 3.75 Å/mm. The resolution was regulated by adjusting entrance and exit slits. These were typically set at a width of .150 mm, resulting in a nominal resolution of .04 Å. The source of radiation was a Hinteregger hydrogen discharge lamp.

The McPherson monochromator was modified to allow double-beam operation by placing a MgF₂ Rochon polarizing prism (Karl Lambrecht) after the exit slit, thereby splitting the beam. One beam was passed through the sample cell to an end-on photomultiplier tube (EMI-Gencom 9635QB), as had been the case with single beam operation. The second beam was reflected from a MgF₂-coated aluminum front-surface mirror (Acton Research) into a side-on photomultiplier tube (Hamamatsu R106UH). The phototube currents were transmitted to electrometers, the signal output of which were sent to a computer (TRS-80 Model I) through a 12-bit A/D converter (Teledyne 7109). This A/D converter was a dual slope type which integrated data over a fixed time period; this period was set at .25 seconds. Knowledge of photomultiplier tube parameters allowed the conversion of the signal to the number of photons collected during integration. The statistical signal/noise ratio (S:N) could then be calculated by

\[ S:N = \sqrt{\# \text{ photons collected}} \]
Hence the number of integration periods required for a specified S:N ratio could be readily determined. In this experiment the S:N ratio was fixed at 500:1. The computer was programmed to perform the task of S:N ratio determination as well as to store the averaged signals on a disk.

The instrument was converted to a double beam system in order to compensate for light-intensity fluctuations. The precise wavelength control required by this experiment also necessitated the incorporation of a stepper motor (North American Philips K82501-P1) into the monochromator scan drive. The stepper motor (48 steps/rev) replaced the 200 rev/min synchronous motor previously used to drive the worm gear which rotated at 25 Å/rev. The gear chain, already in place, was set for a gear reduction of 500:1. The stepper motor operating with this setting took 960 steps/Å. The operation of the stepper motor, and thus of the grating drive, was controlled through the micro-computer.

A sample cell with a path length of 23 cm was equipped with 2 mm quartz windows (S1-UV, Esco Products Inc.) capable of transmitting useable light intensity to ca. 1700 Å. The cell was constructed of 1/2" thick aluminum to withstand high pressure gradients. The plumbing, window mounting and cell assembly were such that both high vacuum and high pressure could be maintained.

All samples were studied in the vapor phase at absorber pressures of less than 2.5 x 10^{-2} torr. High quality methyl iodide (Aldrich) was further purified by several vacuum distillations consisting of successive freeze-pump-thaw cycles. The sample pressure in the cell was measured using a differential-pressure transducer (Validyne Engineering
DP-103). Monitoring of the sample cell pressure as SF$_6$ (Matheson, 99.99% purity) was added was accomplished with another pressure transducer (Validyne Engineering DP-15).

Once an appropriate CH$_3$I pressure was obtained in the sample cell an unperturbed absorption spectrum was recorded. This same CH$_3$I sample remained in the cell throughout the experiment. SF$_6$ was then introduced into the cell in increments of approximately .5 bar until total SF$_6$ pressure reached ca. 5.0 bar. At each increment an absorption spectrum was taken; thus a set of $A^p(\bar{\nu})$'s, absorption spectra with perturbation applied, was obtained. A moment analysis technique was utilized to calculate numerical values for the coefficients $C_0$, $C_1$ and $C_2$ (Eq. 16, 17 and 18) at each perturbation pressure.

To understand how this moment analysis was applied, a number of quantities must be defined. The moments of the unperturbed spectra are defined as

$$M^n_o = \int A^o(\bar{\nu})\bar{\nu}^n/\bar{\nu} \, d\bar{\nu}. \quad (20)$$

Likewise, moments of the spectra with perturbation applied are

$$M^n_p = \int A^p(\bar{\nu})\bar{\nu}^n/\bar{\nu} \, d\bar{\nu}. \quad (21)$$

Combination of Equations 1, 20 and 21 yield the following:

$$M^n_o \equiv \int A^o(\bar{\nu})/\bar{\nu} \, d\bar{\nu} = C_0 \int A^o(\bar{\nu})/\bar{\nu} \, d\bar{\nu} + C_1 \int \frac{dA^o(\bar{\nu})}{d\bar{\nu}} \, d\bar{\nu} + C_2 \int \frac{d^2A^o(\bar{\nu})}{d\bar{\nu}^2} \, d\bar{\nu}. \quad (22)$$

At the limits the absorbance equals zero and thus the last two integrals are also zero, leaving

$$M^n_o = C_0 \int A^o(\bar{\nu})/\bar{\nu} \, d\bar{\nu} = C_0 M^n_o. \quad (23)$$
Similarly,

\[
M_1^P = \int A^P(\tilde{v})d\tilde{v} = C_0\int A^0(\tilde{v})d\tilde{v} + C_1\int \tilde{v}\frac{dA^0(\tilde{v})}{d\tilde{v}} d\tilde{v} + C_2\int \tilde{v}^2\frac{d^2A^0(\tilde{v})}{d\tilde{v}^2} d\tilde{v}
\]

or

\[
M_1^P = C_0M_0^o + C_1\int \tilde{v}\frac{dA^0(\tilde{v})}{d\tilde{v}} d\tilde{v} + C_2\int \tilde{v}^2\frac{d^2A^0(\tilde{v})}{d\tilde{v}^2} d\tilde{v}.
\]

Integrating these by parts and evaluating at the limits yields

\[
M_1^P = C_0M_0^o - C_1M_0^o
\]

or

\[
C_1 = \frac{C_0M_0^o - M_1^P}{M_0^o}.
\]

Lastly,

\[
M_2^P = \int A^P(\tilde{v})\tilde{v} d\tilde{v} = C_0\int A^0(\tilde{v})d\tilde{v} + C_1\int \tilde{v}^2\frac{dA^0(\tilde{v})}{d\tilde{v}} d\tilde{v} + C_2\int \tilde{v}^3\frac{d^2A^0(\tilde{v})}{d\tilde{v}^2} d\tilde{v}
\]

or

\[
M_2^P = C_0M_0^o + C_1\int \tilde{v}^2\frac{dA^0(\tilde{v})}{d\tilde{v}} d\tilde{v} + C_2\int \tilde{v}^3\frac{d^2A^0(\tilde{v})}{d\tilde{v}^2} d\tilde{v}.
\]

Again, applying integration by parts and evaluating at the limits gives

\[
M_2^P = C_0M_0^o - 2C_1M_1^o + 2C_2M_0^o
\]

or

\[
C_2 = \frac{M_2^P - C_0M_0^o + 2C_1M_1^o}{2M_0^o}.
\]
To illustrate the use of this technique a hypothetical absorption curve is assumed. The curve used is a modified Gaussian function because of its simple analytic form. The absorption spectra are expressed as

\[ A^o(\tilde{\nu}) \equiv A^o_{\text{max}} \frac{\tilde{\nu}}{\tilde{\nu}_o} e^{-\left(\tilde{\nu} - \tilde{\nu}_o\right)^2/\alpha^2} \]

and

\[ A^p(\tilde{\nu}) \equiv A^p_{\text{max}} \frac{\tilde{\nu}}{\tilde{\nu}_o} e^{-\left(\tilde{\nu} - \tilde{\nu}_o\right)^2/\alpha'{}^2} , \]

where \( \tilde{\nu}_o \) is the wave number of the band maximum and

\[ \alpha \equiv \sqrt{\text{(half-width)}^2/\ln 2} . \]

Utilizing these definitions the moments can be easily calculated. Only the results are given here.

\[ M^o_o = A^o_{\text{max}} \frac{\alpha}{\tilde{\nu}_o} \sqrt{\pi} , \]

\[ M^o_1 = A^o_{\text{max}} \alpha \sqrt{\pi} , \]

\[ M^o_2 = A^o_{\text{max}} \frac{\alpha}{\tilde{\nu}_o} \sqrt{\pi} \left( \frac{\alpha^2}{2} + \tilde{\nu}_o^2 \right) , \]

and

\[ M^p_o = A^p_{\text{max}} \frac{\alpha'}{\tilde{\nu}_o} \sqrt{\pi} , \]

\[ M^p_1 = A^p_{\text{max}} \alpha' \sqrt{\pi} , \]

\[ M^p_2 = A^p_{\text{max}} \frac{\alpha'}{\tilde{\nu}_o} \sqrt{\pi} \left( \frac{\alpha'^2}{2} + \tilde{\nu}_o^2 \right) . \]

These moments, in combination with Equations 22, 23 and 24, give the coefficients;
\[ C_0 = \frac{A_P^{\max} \alpha' \tilde{\nu}_o}{A_0^{\max} \alpha \tilde{\nu}_o}, \]

\[ C_1 = \frac{A_P^{\max} \alpha'}{A_0^{\max} \alpha} (\tilde{\nu}_o - \tilde{\nu}_o') = C_0 (\tilde{\nu}_o - \tilde{\nu}_o') \]

and

\[ C_2 = \frac{A_P^{\max} \alpha'}{2A_0^{\max} \alpha} \left[ \alpha'^2 - \alpha^2/2 + (\tilde{\nu}_o' - \tilde{\nu}_o)^2 \right] = \frac{C_0}{2} \left[ \alpha'^2 - \alpha^2/2 + (\tilde{\nu}_o' - \tilde{\nu}_o)^2 \right]. \]

It should be apparent that \( C_1 \) is primarily dependent on the energy shift whereas \( C_2 \) is dependent on both the energy shift and band broadening. Although the explicit form of these coefficients changes with the definition of \( A_0(\tilde{\nu}) \) and \( A^P(\tilde{\nu}) \), the dependency on the energy shift and band broadening is retained.

In actuality the integrations were performed numerically utilizing a Newton-Cotes-8-point technique. The integration was performed on the TRS 80 micro-computer. A copy of the program can be found in Appendix D.
Data and Results

Experimental data were compiled on the first s-Rydberg state of CH$_3$I in the presence of the foreign gas SF$_6$. Additional experimental systems explored by Altenoh et al. were also analyzed in the context of this model. These results will be reviewed as well.

All CH$_3$I/SF$_6$ data sets were run from ca. 2007Å to 2221Å; the band maximum of the CH$_3$I spectrum before perturbation was 2011.6Å. Figure 3 shows a typical spectral series of CH$_3$I with SF$_6$. Introduction of SF$_6$ to the sample cell resulted in a slight red shift of the CH$_3$I band maximum. An asymmetry in the broadening, observable at approximately 4.0 bar, becomes more pronounced as SF$_6$ pressure is increased. Intensity of the absorption peak falls off proportionately as the band broadens to lower frequencies. An isobestic point, where the absorption remains a constant, is observable on each side of the band maximum.

Three spectral series of CH$_3$I pressurized with SF$_6$, designated as sets A, B and C, are reviewed here. Spectra were analyzed using a moment analysis, as outlined in the previous section, to yield a set of coefficients for each spectral series (Table 1). Figures 4 through 7 show plots of these coefficients versus pressure. For sets A and B a data point was taken every 0.05Å whereas for set C one was taken every 0.1Å. Two results are strikingly obvious. First, the value of C$_0$ rarely varies from 1.0 by more than 4 percent at pressures less than 5 bar. Secondly, the plots of C$_1$ and C$_2$ both yield essentially straight lines with r$^2$ values never less than .96 and usually greater than .98,
Figure 3. Example of increasing SF$_6$ pressure on the 2011.6Å band of methyl iodide. Pressures were: neat, 1.133 bar, 1.985 bar, 2.94 bar, 4.12 bar and 5.065 bar.
<table>
<thead>
<tr>
<th>Data Set</th>
<th>Pressure</th>
<th>$C_0$</th>
<th>$C_1$</th>
<th>$C_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.065</td>
<td>1.016</td>
<td>1.92</td>
<td>38.4</td>
</tr>
<tr>
<td>A</td>
<td>2.136</td>
<td>.986</td>
<td>4.48</td>
<td>34.8</td>
</tr>
<tr>
<td>A</td>
<td>3.328</td>
<td>.994</td>
<td>6.91</td>
<td>133</td>
</tr>
<tr>
<td>A</td>
<td>4.611</td>
<td>.968</td>
<td>12.73</td>
<td>255</td>
</tr>
<tr>
<td>A</td>
<td>6.018</td>
<td>.943</td>
<td>14.96</td>
<td>326</td>
</tr>
<tr>
<td>A</td>
<td>7.525</td>
<td>.886</td>
<td>17.54</td>
<td>392</td>
</tr>
<tr>
<td>B</td>
<td>1.184</td>
<td>1.033</td>
<td>2.69</td>
<td>97.6</td>
</tr>
<tr>
<td>B</td>
<td>1.581</td>
<td>1.019</td>
<td>2.62</td>
<td>63.3</td>
</tr>
<tr>
<td>B</td>
<td>2.27</td>
<td>1.040</td>
<td>4.26</td>
<td>134</td>
</tr>
<tr>
<td>B</td>
<td>2.78</td>
<td>1.049</td>
<td>4.71</td>
<td>185</td>
</tr>
<tr>
<td>B</td>
<td>3.35</td>
<td>1.042</td>
<td>5.55</td>
<td>200</td>
</tr>
<tr>
<td>B</td>
<td>3.98</td>
<td>1.031</td>
<td>6.42</td>
<td>233</td>
</tr>
<tr>
<td>B</td>
<td>4.49</td>
<td>1.044</td>
<td>8.31</td>
<td>313</td>
</tr>
<tr>
<td>B</td>
<td>5.20</td>
<td>1.029</td>
<td>9.40</td>
<td>351</td>
</tr>
<tr>
<td>C</td>
<td>1.133</td>
<td>1.012</td>
<td>2.47</td>
<td>39.2</td>
</tr>
<tr>
<td>C</td>
<td>1.985</td>
<td>1.017</td>
<td>3.82</td>
<td>75.7</td>
</tr>
<tr>
<td>C</td>
<td>2.94</td>
<td>1.019</td>
<td>6.19</td>
<td>144</td>
</tr>
<tr>
<td>C</td>
<td>4.12</td>
<td>1.013</td>
<td>9.19</td>
<td>270</td>
</tr>
<tr>
<td>C</td>
<td>5.065</td>
<td>1.005</td>
<td>11.10</td>
<td>336</td>
</tr>
</tbody>
</table>
where $r$ is the correlation coefficient. Only one plot, $C_2$ of set $C$, shows any substantial deviation from linearity. In particular, this plot appears to be quadratic, a stark anomaly with respect to previous experimental data. Further investigation revealed the problem to be in the baseline adjustment; error associated with baseline adjustment will be discussed in detail later.

Figures 8 and 9 show the correlation of the experimental coefficients for all three spectral series. The agreement is good for $C_1$ at low pressures, but the sensitivity of $C_2$ to parameter adjustments is evident. Figures 10 and 11 show the best fit of the data when all spectral series are plotted together. Again, a straight line results and although the $r^2$ values are diminished somewhat, the fits are still quite reasonable.

Several additional sets of data, comprised of thiirane with various foreign gases, were made available by North Texas State University. These data provided an opportunity to test the model using a number of different perturber gas systems with the same absorbing molecule. The plotted spectra, shown in Figures 12, 13 and 14 of thiirane with $SF_6$, argon and $CF_4$, proved to be the most reliable and thus were chosen for analysis. However, all the thiirane data sets had been run without a baseline. In order to compensate for the lack of an experimental baseline it was necessary to assume that the absorption was zero at the boundaries of the spectrum. A straight line was drawn from one perimeter of the spectra to the other and the area under the peak integrated. The next several figures (15 through 26) show the plots of the
experimental coefficients versus pressure. The results are tabulated in Table 2.

One high pressure experimental data set was looked at to see where the linearity for that particular system could be expected to break down. Thiirane perturbed with SF₆ constituted the most data, and thus was used for analysis. The spectra and coefficient plots are shown in Figures 27, 28, 29 and 30. The rather abrupt change in the curvature would seem to indicate the breakdown of the model. However, the integration is likely to be inaccurate since the band appears to have broadened out of the region of analysis (see Figure 27 on page 45).
<table>
<thead>
<tr>
<th>Thirane w/</th>
<th>Pressure</th>
<th>( C_0 )</th>
<th>( C_1 )</th>
<th>( C_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SF(_6)</strong></td>
<td>1.013</td>
<td>.9309</td>
<td>7.31</td>
<td>199</td>
</tr>
<tr>
<td></td>
<td>1.321</td>
<td>.9265</td>
<td>9.79</td>
<td>313</td>
</tr>
<tr>
<td></td>
<td>1.703</td>
<td>.8680</td>
<td>9.80</td>
<td>405</td>
</tr>
<tr>
<td></td>
<td>2.047</td>
<td>.8576</td>
<td>13.06</td>
<td>499</td>
</tr>
<tr>
<td></td>
<td>2.392</td>
<td>.8642</td>
<td>15.89</td>
<td>661</td>
</tr>
<tr>
<td></td>
<td>3.082</td>
<td>.8411</td>
<td>19.95</td>
<td>983</td>
</tr>
<tr>
<td></td>
<td>3.771</td>
<td>.8134</td>
<td>23.58</td>
<td>1199</td>
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<td></td>
<td>4.460</td>
<td>.7916</td>
<td>27.27</td>
<td>1462</td>
</tr>
<tr>
<td></td>
<td>5.150</td>
<td>.7693</td>
<td>30.62</td>
<td>1733</td>
</tr>
<tr>
<td></td>
<td>5.839</td>
<td>.7484</td>
<td>34.07</td>
<td>2042</td>
</tr>
<tr>
<td></td>
<td>6.529</td>
<td>.7242</td>
<td>36.93</td>
<td>2260</td>
</tr>
<tr>
<td><strong>Ar</strong></td>
<td>3.082</td>
<td>.8509</td>
<td>8.15</td>
<td>225</td>
</tr>
<tr>
<td></td>
<td>7.218</td>
<td>.8356</td>
<td>9.96</td>
<td>603</td>
</tr>
<tr>
<td></td>
<td>9.287</td>
<td>.8506</td>
<td>11.92</td>
<td>864</td>
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<td></td>
<td>11.355</td>
<td>.8177</td>
<td>13.83</td>
<td>992</td>
</tr>
<tr>
<td></td>
<td>14.113</td>
<td>.8182</td>
<td>15.39</td>
<td>1302</td>
</tr>
<tr>
<td></td>
<td>16.182</td>
<td>.8112</td>
<td>17.07</td>
<td>1384</td>
</tr>
<tr>
<td></td>
<td>18.250</td>
<td>.8103</td>
<td>18.40</td>
<td>1736</td>
</tr>
<tr>
<td></td>
<td>21.698</td>
<td>.8091</td>
<td>22.00</td>
<td>2122</td>
</tr>
<tr>
<td><strong>CF(_4)</strong></td>
<td>1.013</td>
<td>.9772</td>
<td>-1.03</td>
<td>35.0</td>
</tr>
<tr>
<td></td>
<td>1.358</td>
<td>.9580</td>
<td>-0.13</td>
<td>48.7</td>
</tr>
<tr>
<td></td>
<td>1.702</td>
<td>.9558</td>
<td>1.62</td>
<td>74.9</td>
</tr>
<tr>
<td></td>
<td>2.391</td>
<td>.9642</td>
<td>3.15</td>
<td>139</td>
</tr>
<tr>
<td></td>
<td>3.080</td>
<td>.9054</td>
<td>5.19</td>
<td>158</td>
</tr>
<tr>
<td></td>
<td>3.769</td>
<td>.8794</td>
<td>6.98</td>
<td>293</td>
</tr>
<tr>
<td></td>
<td>5.148</td>
<td>.8513</td>
<td>10.75</td>
<td>434</td>
</tr>
<tr>
<td></td>
<td>6.526</td>
<td>.8230</td>
<td>10.91</td>
<td>461</td>
</tr>
<tr>
<td></td>
<td>7.215</td>
<td>.8192</td>
<td>12.69</td>
<td>570</td>
</tr>
</tbody>
</table>
Figure 4. Plot of the $C_0$ coefficient versus pressure for CH$_3$I perturbed with SF$_6$ from data set B.
Figure 5. Plot of the $C_1$ coefficient versus pressure for CH$_3$I perturbed with SF$_6$ from data set B.
\[ Y = A + B \times X \]

\[ A = 0.888 \]

\[ B = 1.738 \]

\[ R-SQUARE = 0.983 \]

\[ 0.00 \]

\[ +8.00 \]

\[ +4.00 \]

\[ +2.00 \]

\[ 0.00 \]

\[ +1.00 \]

\[ +2.00 \]

\[ +3.00 \]

\[ +4.00 \]

\[ \text{PRESSURE (BAR)} \]
Figure 6. Plot of the $C_2$ coefficient versus pressure for $\text{CH}_3\text{I}$ perturbed with $\text{SF}_6$ from data set B.
Y = A + Bx

R-SQUARE = 0.996

A = 67.106

B = -8.958
Figure 7. Plot of the $C_2$ coefficient versus pressure for CH$_3$I perturbed with SF$_6$ from data set B. Third data point has been deleted.
COEFFICIENTS

\[ Y = A + Bx \]

\[ R^2 = 0.975 \]

\[ A = 0.168 \]

\[ B = 65.828 \]
Figure 8. Comparative plot of the $C_1$ coefficient versus pressure for the three different CH$_3$I perturbed with SF$_6$ data sets.
EXPERIMENTAL C1 COEFFICIENTS SF6/CH3I
Figure 9. Comparative plot of the $C_2$ coefficient versus pressure for the three CH$_3$I perturbed with SF$_6$ data sets.
EXPERIMENTAL C2 COEFFICIENTS SF6/CH3I

PRESSURE (BAR)

COEFFICIENTS
Figure 10. Plot showing best fit of the $C_1$ coefficient versus pressure when all three data sets are plotted together.
$Y = A + BX$

$R^2 = 0.944$

$A = -0.567$

$B = 2.281$
Figure 11. Plot showing best fit of the $C_2$ coefficient versus pressure when all three data sets are plotted together.
Figure 12. Spectra of the 174 nm band of thiirane with increasing SF₆ pressure.
Figure 13. Spectra showing the effects of increasing argon pressure on the 174 nm band of thiirane.
Figure 14. Example of increasing CF$_4$ pressure on the 174 nm band of thiirane.
Figure 15. Plot of the $C_0$ coefficient versus pressure for the 174 nm band of thiirane perturbed with SF$_6$. 
Figure 16. Plot of the $C_1$ coefficient versus pressure for the 174 nm band of thiirane perturbed with SF$_6$. 
Presssure (BAr)

COEFFICIENT

R-Square = 0.993

E = 5.637

X = 1.466

Y = A + BX
Figure 17. Plot of the $C_2$ coefficient versus pressure for the 174 nm band of thiirane perturbed with $SF_6$. 
\[ Y = A + Bx \]

- \( A = -109.418 \)
- \( B = 306.706 \)

**R-Square:** 0.953

**Coefficient:**

- \( X \leq 3 \)
- \( X > 3 \)

**Pressure (Bar):**

- 0.00
- 1.00
- 2.00
- 3.00
Figure 18. Plot of the $C_0$ coefficient versus pressure for the 174 nm band of thiirane perturbed with argon.
Figure 19. Plot of the $C_1$ coefficient versus pressure for the 174 nm band of thiirane perturbed with argon.
\[ Y = A + B \times X \]

\[ A = 2.977 \]

\[ B = 0.889 \]

\[ R\text{-SQUARE} = 0.950 \]
Figure 20. Plot of the $C_1$ coefficient versus pressure of thiirane/argon. The 0,0 data point has been deleted.
Figure 21. Plot of the $C_2$ coefficient versus pressure for the 174 nm band of thiirane with argon.
\[ Y = A + B \cdot X \]

\[ A = -61.782 \]

\[ B = 96.688 \]

\[ R\text{-SQUARE} = 0.992 \]
Figure 22. Plot of the $C_0$ coefficient versus pressure for the 174 nm band of thiirane perturbed with CF$_4$. 
Figure 23. Plot of the $C_1$ coefficient versus pressure for the 174 nm band of thiirane perturbed with CF$_4$. 
$Y = A + Bx$

$R^2 = 0.949$

$A = -1.599$

$B = 2.053$

COEFFICIENT

PRESSURE (BAR)
Figure 24. Plot of the $C_1$ coefficient versus pressure for the 174 nm band of thiirane perturbed with $\text{CF}_4$. The 0,0 data point has been deleted.
Figure 25. Plot of the $C_2$ coefficient versus pressure for the 174 nm band of thiirane perturbed with CF$_4$. 
$Y = A + BX$

$A = -46.599$

$B = 63.242$

$R\text{-SQUARE} = 0.972$
Figure 26. Plot of the $C_2$ coefficient versus pressure for the 174 nm band of thiirane with $CF_4$. The 0,0 data point has been deleted.
$Y = A + B \times X$

$A = -66.290$

$B = 87.299$

$R$-SQUARED = 0.976
Figure 27. Spectra showing high pressure effects of SF₆ on the 174 nm band of thiirane. Pressure was taken up to 21 bar.
Figure 28. Plot of the $C_0$ coefficient versus pressure of the 174 nm band of thiirane at elevated SF$_6$ pressures.
Figure 29. Plot of the $C_1$ coefficient versus pressure of the 174 nm band of thiirane at elevated $SF_6$ pressures.
Figure 30. Plot of the $C_2$ coefficient versus pressure of the 174 nm band of thiirane at elevated $SF_6$ pressures.
Discussion

The focal point of the experiment was the determination of the intermolecular interaction parameters of molecules in excited states. Ground state values for the intermolecular distance and potential-well depth were estimated using Eq.'s 8, 9 and 10. Data on force constants for various molecules in the context of the Lennard-Jones 6,12 potential have been tabulated in Appendix 1A of "Molecular Theory of Gases and Liquids" (7). These force constants were calculated primarily using the second virial coefficient.

The analysis of thiirane perturbed with SF₆, argon and CF₄ posed an additional problem in that no ground-state data on molecular parameters were available for thiirane. Although it was not possible totally to circumvent this problem, useful information was obtained utilizing two different estimates for the ground state.

The first estimate, based on tables from "Data Book on Hydrocarbons" (12) (DBH) was that of the critical constants, T_c and P_c, from the boiling point and molecular weight of thiirane respectively. The second estimate was based on the variation of critical constants of oxygen compounds with their sulfur counterparts. Hence thiirane critical constants were approximated by the adjustment of the critical constants of oxirane based on changes observed for other analogous pairs such as dimethyl ether and dimethyl sulfide. The estimate of critical constants from DBH yielded T_c = 493 K and P_c = 36 atm whereas comparison of critical constants with oxirane gave T_c = 563 K and P_c = 73 atm.
Figure 31. Graph of molecular weight versus critical pressure for normal paraffins. From "Data Book on Hydrocarbons".
The pseudo-critical pressure of light hydrocarbon mixtures having an average molecular wt. less than 80 can be determined from this curve.

Critical Pressure of Normal Paraffins
Figure 32. Graph of the critical temperature of light hydrocarbons versus boiling point. From "Data Book on Hydrocarbons".
Critical Temperature of Light Hydrocarbons
Pure Compounds and Mixtures

The base curve represents critical temperature vs. boiling point for pure hydrocarbons and pseudo-critical temperature vs. molal average boiling point for mixtures.

The gravity curves represent true critical temperature vs. weight average boiling point for mixtures. For all hydrocarbons the paraffin gravity of the same boiling point should be used in computing the gravity of the mixture.

The determination of the molecular parameters from the critical constants is straightforward. For most gases it is a good assumption (7) that
\[ \frac{kT_c}{\varepsilon} = 1.3 \] where \( \varepsilon = D_e \).

Also
\[ b_o = \frac{18.4 T_c}{P_c} \]

and
\[ b_o = \frac{2}{3\pi} \tilde{N} \sigma^3, \] where again \( 2^{1/6} \sigma = r_e \).

Here \( b_o \) is the volume \( (\text{cm}^3/\text{mol}) \) and \( \tilde{N} \) is Avagadro’s number. Values calculated for the ground state of thiirane were \( \sigma(\text{\AA}) = 5.85 \) and \( D_e(\text{cm}^{-1}) = 263.7 \) for DBH and \( \sigma(\text{\AA}) = 4.83 \) and \( D_e(\text{cm}^{-1}) = 301.2 \) for comparison with oxirane. Ground state values for the intermolecular parameters of the systems investigated are given in Table 3.

<table>
<thead>
<tr>
<th>Molecular Combination</th>
<th>( r_e(\text{\AA}) )</th>
<th>( D_e(\text{cm}^{-1}) )</th>
<th>( r_e(\text{\AA}) )</th>
<th>( D_e(\text{cm}^{-1}) )</th>
<th>( r_e(\text{\AA}) )</th>
<th>( D_e(\text{cm}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)/SF(_6)</td>
<td>5.705 198.4</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Thiirane/SF(_6)</td>
<td>—</td>
<td>—</td>
<td>6.38 191.9</td>
<td>5.80 205.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thiirane/Ar</td>
<td>—</td>
<td>—</td>
<td>5.19 149.5</td>
<td>4.62 159.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thiirane/CF(_4)</td>
<td>—</td>
<td>—</td>
<td>5.42 164.8</td>
<td>4.85 176.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Once the experimental coefficients were determined, calculation of the excited-state parameters was accomplished using the TRS-80 micro-computer. The program, "Matrix 2/Bas", utilized three different methods to aid in the data analysis.

Initially, data is put into matrix form. This is accomplished by rearrangement of Eq. 17 to give

\[ 0 = (C_1 F_{-3} + 2D_e F_{-1} - D_e F_1)1/D_e' - (2/r_e^6 F_{-1})r_e^6 + (1/r_e^{12} F_1)r_e^{12} \]

or

\[ 0 = a(1/D_e') - br_e^6 + cr_e^{12} \]

Considering three pressures at a time gives the following matrix equation.

\[
\begin{bmatrix}
a & b & c \\
a' & b' & c' \\
a'' & b'' & c''
\end{bmatrix}
\begin{bmatrix}
1/D_e' \\
r_e^6 \\
r_e^{12}
\end{bmatrix}
= 0
\]

This will be true if and only if

\[
\begin{bmatrix}
a & b & c \\
a' & b' & c' \\
a'' & b'' & c''
\end{bmatrix}
= 0.
\]

Therefore, the determinants should be equal to zero if the values for the ground state are correct. The values of the determinants can then be used as a measurement of the accuracy of the data even though they
yield no specific values for \( r_e' \) and \( D_e' \). Determinants were calculated for all permutations of pressures within a data set. It was found that while the determinants equal zero theoretically, they can become quite large when even modest errors are introduced. For a complete discussion of the determinants and variation associated with errors in the ground state and coefficients, see Appendix E.

The second part of the program calculates values for \( r_e' \) and \( D_e' \) by using Eq. 17 at two different perturber gas pressures. This was done for all possible pairs of pressures. Lastly, the program determines \( r_e' \) and \( D_e' \) from Eq.'s 17 and 18 at each pressure. Theoretically these methods yield the same numerical values for \( r_e' \) and \( D_e' \). In actuality the first method proved to be exceedingly sensitive to errors associated with the coefficients and the numbers were discarded.

Presuming the potential energy curve of an excited state is independent of the specific pressure of the perturber gas, each pressure should give the same values of \( r_e' \) and \( D_e' \). Realistically, this does not quite hold true for experimental systems. Table 4 lists the interaction parameters of \( CH_3I \) perturbed with \( SF_6 \). Values obtained at each pressure were averaged to give the final \( r_e' \) and \( D_e' \) for each data set. In turn, these values were also averaged to show a final decrease in the intermolecular distance from \( 5.705 \AA \) to \( 5.58 \AA \) and a substantial increase in the potential well depth from 198.4 cm\(^{-1}\) to 253 cm\(^{-1}\). This represents a change of only 2.2% in the intermolecular distance while giving a 27.5% change in the potential well depth.

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Table 4

CH$_3$I with SF$_6$

<table>
<thead>
<tr>
<th>Data Set</th>
<th>Pressure (Bar)</th>
<th>$r_e$ (Å)</th>
<th>$D_e$ (cm$^{-1}$)</th>
<th>$\Delta r_e$ (Å)</th>
<th>$\Delta D_e$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.065</td>
<td>5.59</td>
<td>240.8</td>
<td>-0.115</td>
<td>42.4</td>
</tr>
<tr>
<td>A</td>
<td>2.136</td>
<td>----------</td>
<td>--------</td>
<td>---------------</td>
<td>-------------------------</td>
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<tr>
<td>A</td>
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<tr>
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<td>5.61</td>
<td>259.9</td>
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</tr>
<tr>
<td>A</td>
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<td>5.61</td>
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</tr>
<tr>
<td></td>
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<tr>
<td></td>
<td>(±.02)</td>
<td>(±8.9)</td>
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<tr>
<td>B</td>
<td>1.184</td>
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</tr>
<tr>
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</tr>
<tr>
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<tr>
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<td>250.8</td>
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<td>52.4</td>
</tr>
<tr>
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<td>-0.185</td>
<td>59.3</td>
</tr>
<tr>
<td>B</td>
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<td>256.8</td>
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<tr>
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<td>C</td>
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<tr>
<td>C</td>
<td>5.065</td>
<td>5.54</td>
<td>260.1</td>
<td>-0.165</td>
<td>61.7</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>5.58</td>
<td>251.6</td>
<td>-0.127</td>
<td>53.2</td>
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<tr>
<td></td>
<td>(±.04)</td>
<td>(±7.8)</td>
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</tbody>
</table>

Average of the three sets

5.58  253.0  -0.131  54.6

(±.02)  (±4.4)
Table 5 gives the values of $r_e'$ and $D_e'$ for thiirane with the various perturbers. As could be expected, based on the size of the individual molecules themselves, $r_e'$ values were largest for thiirane with SF$_6$ followed by CF$_4$ and lastly argon. However, the change of the intermolecular distance between the ground state and the excited state, $\Delta r_e'$, was substantially greater for argon than for either SF$_6$ or CF$_4$. This too is likely attributable to argon's small size and ability to approach the thiirane molecule closely without significant electron cloud overlap. Interestingly, the $\Delta r_e'$ values for SF$_6$ and CF$_4$ were almost equal. Relative changes of the intermolecular distance for SF$_6$, argon and CF$_4$, when ground-state estimates were based on DBH, were 4.1%, 8.1% and 4.2%, respectively. Analogously, percent changes when ground states were estimated by comparison with oxirane for the same molecules were 3.5%, 8.7% and 4.5%, respectively.

Ground state $D_e$ values vary with the polarizability ($\alpha$) of the perturbing gas molecule. However, in the excited state the dependence on the electron affinity (EA) of the perturber becomes apparent. From Tables 5 and 6 it can be seen that SF$_6$ has both the greatest polarizability and EA and likewise displays the largest $D_e$, $D_e'$ and $\Delta D_e'$ values. Although the polarizability and ground-state potential-well depth are greater for CF$_4$, $D_e'$ and $\Delta D_e'$ are both larger for argon which has a larger EA.
Table 5

<table>
<thead>
<tr>
<th>Thiirane Pressure with Oxirane</th>
<th>DB on H</th>
<th>Comparison with Oxirane</th>
</tr>
</thead>
<tbody>
<tr>
<td>w/ (Bar)</td>
<td>( r_e' (\text{Å}) )</td>
<td>( D_e' (\text{cm}^{-1}) )</td>
</tr>
<tr>
<td>SF6</td>
<td>1.013</td>
<td>-----</td>
</tr>
<tr>
<td></td>
<td>1.321</td>
<td>6.31</td>
</tr>
<tr>
<td></td>
<td>1.703</td>
<td>6.14</td>
</tr>
<tr>
<td></td>
<td>2.047</td>
<td>6.19</td>
</tr>
<tr>
<td></td>
<td>2.392</td>
<td>6.17</td>
</tr>
<tr>
<td></td>
<td>3.082</td>
<td>6.10</td>
</tr>
<tr>
<td></td>
<td>3.771</td>
<td>6.09</td>
</tr>
<tr>
<td></td>
<td>4.460</td>
<td>6.07</td>
</tr>
<tr>
<td></td>
<td>5.150</td>
<td>6.05</td>
</tr>
<tr>
<td></td>
<td>5.839</td>
<td>6.02</td>
</tr>
<tr>
<td></td>
<td>6.529</td>
<td>6.01</td>
</tr>
<tr>
<td>Avg</td>
<td>6.12</td>
<td>316.7</td>
</tr>
<tr>
<td></td>
<td>(±.09)</td>
<td>(±13.8)</td>
</tr>
<tr>
<td>Ar</td>
<td>3.082 [5.06]</td>
<td>236.7 [-.13]</td>
</tr>
<tr>
<td>7.218</td>
<td>4.84</td>
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<tr>
<td>9.287</td>
<td>4.79</td>
<td>235.9</td>
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<td>11.355</td>
<td>4.80</td>
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<td>14.113</td>
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<td>235.7</td>
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<td>16.182</td>
<td>4.77</td>
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<tr>
<td>18.250</td>
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<tr>
<td>21.698</td>
<td>4.70</td>
<td>241.9</td>
</tr>
<tr>
<td>Avg</td>
<td>4.77</td>
<td>235.2</td>
</tr>
<tr>
<td>(±0.05)</td>
<td>(±4.1)</td>
<td>(±0.05)</td>
</tr>
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</table>
Table 5 (continued)

<table>
<thead>
<tr>
<th>Thiirane Pressure w/ (Bar)</th>
<th>DB on H</th>
<th>Comparison with Oxirane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$r_e' \quad (\text{cm}^{-1})$</td>
<td>$\Delta r_e' \quad (\text{cm}^{-1})$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF$_4$</td>
<td>1.013</td>
<td>5.20 [155.4]</td>
</tr>
<tr>
<td></td>
<td>1.358</td>
<td>5.19 180.7</td>
</tr>
<tr>
<td></td>
<td>1.702</td>
<td>5.20 206.3</td>
</tr>
<tr>
<td></td>
<td>2.391</td>
<td>5.18 219.0</td>
</tr>
<tr>
<td></td>
<td>3.080</td>
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<td></td>
<td>3.769</td>
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<td>5.148</td>
<td>5.18 243.1</td>
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<td></td>
<td>6.526</td>
<td>5.17 232.9</td>
</tr>
<tr>
<td></td>
<td>7.215</td>
<td>5.16 238.4</td>
</tr>
<tr>
<td>Avg (±.02) (±20.7)</td>
<td>5.19</td>
<td>222.4</td>
</tr>
<tr>
<td>(±.01) (±24.7)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: Points inside parentheses [ ] were calculated to be invalid using a standard Q test at a 90% confidence level or because of physical impossibility when compared with appropriate absorption spectrum.
The relative changes in the potential-well depths were substantially greater than those previously seen with CH$_3$I. For SF$_6$, Ar and CF$_4$ the changes were 65%, 57.3% and 34.9%, respectively, when the ground state estimates were based on DBH. For comparison with oxirane the changes were 70%, 70.8% and 40.9%, respectively, for the same molecules. The larger relative change in the well depth exhibited between the ground and excited states of thiirane implies a greater susceptibility to perturbation than was seen with CH$_3$I.

Theoretical plots were calculated using the average values of $r_e'$ and $D_e'$ obtained for the corresponding experimental data set. Thus, $r_e'$, $r_e''$, $D_e$ and $D_e'$ values were used to calculate a new set of theoretical coefficients using Eq.'s 17 and 18. These calculated coefficients were then plotted versus pressure. Comparison of the theoretically calculated coefficients with those determined experimentally, figures 33 through 40, in general showed good agreement. In addition, these comparative plots help identify invalid experimental data points.

Various potential sources of error exist in the experiment, even with the modifications detailed in the experimental section. The least-predictable source of error arose from the bulging of the windows as

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Polarizability ($\alpha$)</th>
<th>Electron Affinity (KJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF$_6$</td>
<td>6.5</td>
<td>138</td>
</tr>
<tr>
<td>Ar</td>
<td>1.6</td>
<td>-35</td>
</tr>
<tr>
<td>CF$_4$</td>
<td>3.9</td>
<td>-49</td>
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</tbody>
</table>

Table 6
Figure 33. Plot of both the experimental and theoretical $C_1$ coefficients versus pressure for CH$_3$I perturbed with SF$_6$. 
Figure 34. Plot showing the correlation between the experimental and theoretical $C_2$ coefficients (versus pressure) for CH$_3$I perturbed with SF$_6$. 
Figure 35. Plot showing the correlation between the experimental and theoretical $C_1$ coefficients for thiirane perturbed with $SF_6$. Diamonds – DBH; triangles – comparison with oxirane.
Figure 36. Plot showing the correlation between the experimental and theoretical $C_2$ coefficients for thiirane perturbed with $SF_6$. Diamonds give the theoretical curve for ground-state estimates based on DBH. Triangles give the analogous curve for a ground-state estimate based on comparison with oxirane.
Figure 37. Plot of the experimental and theoretical $C_1$ coefficients for thiirane perturbed with argon. Diamonds represent a ground state estimate based on DBH. Ground state estimate based on comparison with analogous oxygen compound represented by triangles.
Figure 38. Plot of the experimental and theoretical $C_2$ coefficients for thiirane perturbed with argon. Ground state estimate based on DBH represented by diamonds, by comparison with oxirane represented by triangles.
Figure 39. Plot of the experimental and theoretical $C_1$ coefficients for thiirane perturbed with CF$_4$. Diamonds give the theoretical curve for a ground state estimate based on DBH. Squares give the same curve for a ground state estimate based on comparison with oxirane.
Figure 40. Plot of the experimental and theoretical $C_2$ coefficients for thiirane perturbed with $\text{CF}_4$. Diamonds give the theoretical curve for a ground state estimate based on DBH. Squares give the analogous curve for a ground state estimate based on comparison with oxirane.
perturber gas pressure was increased, causing displacement along the absorbance axis. While the stepper motor ensured that the spectrum was run over precisely the same region, there was no way to restrict displacement along the absorbance axis. Hence the baseline was shifted up or down the axis to bring it into the closest possible alignment to each absorption spectrum.

This process involved taking the average difference between the baseline and absorption spectrum of the first twenty data points to calculate the required offset. The decision to use twenty data points was relatively arbitrary, one of the main objectives being consistency. However, enough points needed to be used to enable an accurate average to be determined without using so many points that at high pressure the absorption peak might broaden into the region. Table 7 shows the difference in the offset estimate after 10, 20 and 30 data points and the resulting variation in the coefficients. Even small changes in the offset (i.e., <0.0005 au) showed a marked effect on coefficient values. The $C_2$ coefficient was particularly sensitive, although the variation in values caused by using 20 versus 30 data points was usually less than 10%.

An additional source of error resulted from the static noise associated with both the absorption spectrum and baseline. The following equations can be defined

$$I_t = I_t^o(1 \pm S:N^{-1})$$ for transmitted light

$$I_i = I_i^o(1 \pm S:N^{-1})$$ for incident light
It is also known that

\[ \text{Absorbance} = \log \frac{I_i}{I_t} = \log \frac{I^o_i}{I^o_t} + \log \left( \frac{1 \pm S:N^{-1}}{1 \pm S:N^{-1}} \right) \]

From the propagation of errors (14) we get the following result:

\[ \sigma_A^2 = (\frac{\partial A}{\partial I_t})^2 \sigma_{I_t}^2 + (\frac{\partial A}{\partial I_i})^2 \sigma_{I_i}^2 \]

or

\[ \sigma_A^2 = (\frac{\partial \log I_i/I_t}{\partial I_t})^2 \sigma_{I_t}^2 + (\frac{\partial \log I_i/I_t}{\partial I_i})^2 \sigma_{I_i}^2 \]

After taking the partial derivatives the equation becomes

\[ \sigma_A^2 = \left( \frac{-1}{2.303 I_t} \right)^2 \sigma_{I_t}^2 + \left( \frac{1}{2.303 I_i} \right)^2 \sigma_{I_i}^2 \]

Since

\[ \sigma_{I_t} = I_t (S:N)_t^{-1} \]

and

\[ \sigma_{I_i} = I_i (S:N)_i^{-1} \]

then

\[ \sigma_A^2 = \left( \frac{-1}{2.303} \right)^2 + \left( \frac{1}{2.303} \right)^2 \]

The S:N ratio was set at

\[ (S:N)_t = (S:N)_i = 500:1 \]

giving

\[ \sigma_A = \sqrt{2(S:N)^{-1}/2.303} = \sqrt{2(500:1)^{-1}/2.303} = 1.228 \times 10^{-3} \text{ a.u.} \]
for each point in the spectrum. Since a baseline was subtracted from each spectrum to give the actual absorbance the standard deviation would be

\[ \sigma = 2(S:N)^{-1/2} \times 2.303 = 2(500:1)^{-1/2} \times 2.303 = 1.737 \times 10^{-3} \text{ a.u.} \]

for any given data point. However each spectrum consisted of over 400 data points and since this error is random, the effects would tend to cancel out in the integration.

In an attempt to quantify the numerical error in the coefficients associated with these factors a series of neat CH\(_3\)I spectra was run. This set of spectra, termed A\(_1\), A\(_2\) and A\(_3\), consisted of three consecutive spectra taken on the same CH\(_3\)I sample under virtually identical laboratory conditions. If \( D_e = D_e' \) and \( r_e = r_e' \), as would be the case when no perturbation was applied, the expected coefficient values would be \( C_0 = 1 \), \( C_1 = 0 \) and \( C_2 = 0 \). By comparing the various A\(_0\) spectra to one another it was found that a variation of ±0.02 cm\(^{-1}\) for \( C_1 \) and of ±10 cm\(^{-2}\) for \( C_2 \) could be expected due to baseline adjustment and noise. Other possible sources of error associated with the instrumentation are thought to be negligible in comparison with those sources mentioned.
<table>
<thead>
<tr>
<th>Pressure (Bar)</th>
<th>10 points</th>
<th>20 points</th>
<th>30 points</th>
<th>Coefficient value after</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.133</td>
<td>-5.317D^{-3}</td>
<td>-5.814D^{-3}</td>
<td>-5.950D^{-3}</td>
<td>C₀ 1.018</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C₁ 2.832</td>
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<td></td>
<td></td>
<td></td>
<td>C₂ 77.56</td>
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<tr>
<td>1.985</td>
<td>-7.475D^{-3}</td>
<td>-7.644D^{-3}</td>
<td>-7.543D^{-3}</td>
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<td></td>
<td></td>
<td></td>
<td>C₁ 3.941</td>
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<td></td>
<td></td>
<td></td>
<td>C₂ 88.66</td>
</tr>
<tr>
<td>2.94</td>
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<td>-8.516D^{-3}</td>
<td>-8.351D^{-3}</td>
<td>C₀ 1.025</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>C₁ 6.598</td>
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<td>C₂ 186.8</td>
</tr>
<tr>
<td>4.12</td>
<td>-9.452D^{-3}</td>
<td>-.0100</td>
<td>-.0103</td>
<td>C₀ 1.020</td>
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<td>C₁ 9.593</td>
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<td>-9.955D^{-3}</td>
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<td>C₁ 11.40</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C₂ 367.7</td>
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</table>
Conclusion

The model developed here has proven to be quite capable of giving consistent values for excited state parameters of the first s Rydberg state of CH₃I. Use of the Lennard Jones 6,12 potential was shown to give reasonable and physically relevant values for the intermolecular distance and potential well depth while allowing relative simplicity to be maintained. Coefficients and spectra calculated on the basis of these parameters were in good agreement with those determined experimentally. This holds true until perturber gas pressure is increased to the point where the model seems to break down, probably a result of the broadening of other absorption peaks into the region and/or higher order interactions.

Data pertaining to the 174 nm Rydberg state of thiirane helped to illustrate the wide applicability of the model to various molecular absorber-perturber systems. Comparison of the parameters calculated using the various perturbers allowed for quantization of the strength of interaction of the different molecular systems.
Appendix A

Derivation of equation 1 begins by expressing the perturbed absorbance, \( A^p(\tilde{\nu}) \), as a function of the unperturbed absorbance, \( A^\circ(\nu) \), at a particular frequency, \( \tilde{\nu} \). The perturbation causes the intensity of the band to shift by an amount \( D(Q) \). Therefore \( A^p(\nu) \) receives contributions from \( A^\circ(\tilde{\nu} - \tilde{D}(Q)) \) terms which are weighted by the number of molecules at \( Q \). Since \( \tilde{D}(Q) \) is a continuous variable the equation can be expressed as an integral, leading to

\[
A^p(\tilde{\nu}) = \frac{\int_{Q} \Omega(Q) A^\circ(\tilde{\nu} - \tilde{D}(Q)) dV_Q}{\int_{Q} \Omega(Q) dV_Q}
\]

where \( \Omega(Q) \) is the distribution function. The \( \Omega(Q) \) in the numerator gives the probability of molecules absorbing at \( Q \) while the integral denominator represents the entire distribution.

The above equation is an approximation as the inherent \( \tilde{\nu} \) dependence of absorbance has been neglected. Taking this into consideration produces the following equation.

\[
A^p(\tilde{\nu}) = \frac{\tilde{\nu} \int_{Q} \Omega(Q) A^\circ(\tilde{\nu} - \tilde{D}(Q)) dV_Q}{\int_{Q} \Omega(Q) dV_Q}
\]

The next step is the expansion of \( \frac{A^\circ(\tilde{\nu} - \tilde{D}(Q))}{\tilde{\nu} - D(Q)} \) to change the implicit dependence of \( A^\circ \) on \( \tilde{D}(Q) \) to explicit dependence. Expanding about \( \tilde{\nu} \) with \( \tilde{\nu} - \tilde{D}(Q) \) being the variable gives
\[
\frac{A^\circ (\tilde{\nu} - \tilde{D}(Q))}{\tilde{\nu} - D(Q)} = \frac{A^\circ (\tilde{\nu})}{\tilde{\nu}} + (\tilde{\nu} - \tilde{D}(Q) - \tilde{\nu}) \frac{dA^\circ (\tilde{\nu})/d\tilde{\nu}}{\tilde{\nu}} + \\
\frac{(\tilde{\nu} - \tilde{D}(Q) - \tilde{\nu})^2}{2} \frac{d^2A^\circ (\tilde{\nu})/d\tilde{\nu}^2}{d\tilde{\nu}^2} + \ldots
\]

or

\[
\frac{A^\circ (\tilde{\nu} - \tilde{D}(Q))}{\tilde{\nu} - D(Q)} = \sum_{i=0}^{\infty} (-1)^i \frac{D^i(Q)}{2^i} \frac{d^iA^\circ (\tilde{\nu})/d\tilde{\nu}^i}{d\tilde{\nu}^i}.
\]

From this \(A^p(\tilde{\nu})\) can now be given as

\[
A^p(\tilde{\nu}) = \tilde{\nu} \sum C_1 \frac{dA^\circ (\tilde{\nu})/d\tilde{\nu}}{d\tilde{\nu}^i}
\]

where

\[
C_1 = \frac{(-1)^i}{i!} \frac{\int_{\Omega(Q)} D^i(Q) \, dV_Q}{\int_{\Omega(Q)} \, dV_Q}
\]

which is the desired result.
Appendix B

Upon inspection of the $\Gamma(Q)$ term of the general expression for the coefficients

$$c_i = \frac{(-1)^{i-1}}{i!} \frac{\int_Q \Omega(Q) D^i(Q) \Gamma(Q) \, dv_Q}{\int_Q \Omega(Q) \, dv_Q}$$

it should be realized that $\Gamma(Q)$ can be expressed as

$$\Gamma(Q) = \frac{\langle \psi_{\text{ex}} | \tilde{M} | \psi_{\text{g}} \rangle^2}{\langle \psi_{\text{ex}}^o | \tilde{M}^o | \psi_{\text{g}}^o \rangle^2}.$$

According to perturbation theory the operator would normally be expressed as $\tilde{M} = \tilde{M}^o + \lambda \tilde{M}^i$. Since we are dealing with a transition moment or dipole operator which is primarily unperturbed by the applied pressure perturbation (19), the $\lambda$ term of the operator is assumed to be negligible. Any perturbation effects are now expressed only in the form of the wavefunction. The expression for $\Gamma(Q)$ can now be written as

$$\Gamma(Q) = \frac{\langle \psi_{\text{ex}}^o + \sum_{j=1}^{\infty} \lambda^j \psi_{\text{ex}}(j) | \tilde{M}^o + \sum_{j=1}^{\infty} \lambda^j \psi_{\text{g}}(j) \rangle^2}{\langle \psi_{\text{ex}}^o | \tilde{M}^o | \psi_{\text{g}}^o \rangle^2}.$$

The numerator may be rearranged to give

$$\langle \psi_{\text{ex}}^o | \tilde{M} | \psi_{\text{g}}^o \rangle + \sum_{j=1}^{\infty} \lambda^j \langle \psi_{\text{ex}}(j) | \tilde{M}^o + \sum_{j=1}^{\infty} \lambda^j \psi_{\text{g}}(j) \rangle +$$

$$\langle \psi_{\text{ex}}(j) | \tilde{M}^o + \sum_{j=1}^{\infty} \lambda^j \psi_{\text{g}}(j) \rangle + \sum_{j=1}^{\infty} \lambda^j \langle \psi_{\text{ex}}(j) | \tilde{M} | \psi_{\text{g}}(j) \rangle |^2.$$
Squaring and dropping any term which contains higher than first order corrections gives
\[ |\langle \psi_{ex}^0 | \tilde{M} | \psi_{g}^o \rangle|^2 + \langle \psi_{ex}^0 | \tilde{M} | \psi_{g}^o \rangle [\sum_{j=1}^{\infty} \lambda^j \psi_{ex}^{(j)} | \tilde{M} | \psi_{g}^o \rangle
+ \langle \psi_{ex}^0 | \tilde{M} | \sum_{j=1}^{\infty} \lambda^j \psi_{g}^{(j)} \rangle] \cdot \]

Division by the denominator and again limiting to first order corrections yields
\[ \Gamma(Q) = 1 + \lambda \frac{|\langle \psi_{ex}^0 | \tilde{M} | \psi_{g}^o \rangle|^2}{|\langle \psi_{ex}^0 | \tilde{M} | \psi_{g}^o \rangle|^2} \cdot \]

Even the first order correction would be exceedingly complicated to evaluate. Furthermore, from experimental data we know that the first order correction is negligibly small. At high pressures this correction factor would become increasingly important and would probably require some attempt at evaluation.
From equation 14 in the text, the coefficients appearing in equations 16, 17 and 18 may be derived as follows:

For $C_0$

$$C_0 = (-1)^n \frac{D_r^0}{0!} = \frac{\int_0^R D^0(r) \exp[-U(r)/kT]r^2dr}{\int_0^R \exp[-U(r)/kT]r^2dr} = 1$$

For $C_1$

$$C_1 = (-1)^n \frac{D_r^1}{1!} = \frac{-\int_0^R D^1(r) \exp[-U(r)/kT]r^2dr}{\int_0^R \exp[-U(r)/kT]r^2dr}$$

Using equation 6 gives

$$C_1 = \frac{-\int_0^R D^1(r) \exp[-2D_e(-r_e^6/r^6 + r_e^12/2r^12)/kT]r^2dr}{\int_0^R \exp[-2D_e(-r_e^6/r^6 + r_e^12/2r^12)/kT]r^2dr}$$

The relationship, $b = D_e/kT$, helps to simplify the form. This result, along with the use of equation 12, yields

$$C_1 = -2\int_0^R [D_e (-r_e^6/r^6 + r_e^12/2r^12) - D_e (-r_e^6/r^6 + r_e^12/2r^12)] x \exp[-2b(-r_e^6/r^6 + r_e^12/2r^12)]r^2dr/\int_0^R \exp[-2b(-r_e^6/r^6 + r_e^12/2r^12)]r^2dr$$

Now let

$$x = \frac{r_e^6}{r^6} \text{ or } r^6 = \frac{r_e^6}{x}$$

Then,

$$r^2dr = -\frac{1}{6} r_e^3 x^{-3/2} dx$$

and $C_1$ can be expressed as
\[ C_1 = 2(-\frac{1}{6}r_e^3) \int_{(r_e/R)^6}^\infty [D_e(-\frac{r_e^6 x}{r_e^6} + \frac{r_e^{12} x^2}{2r_e^{12}}) - D_e(-x + \frac{1}{2} x^2)] \times \]

\[ \exp[-2b(-x + \frac{1}{2} x^2)]x^{-3/2} \, dx/ \]

\[ (-\frac{1}{6}r_e^3) \int_{(r_e/R)^6}^\infty \exp[-2b(-x + \frac{1}{2} x^2)]x^{-3/2} \, dx . \]

Multiplying through by the various factors of two gives

\[ C_1 = \int_{(r_e/R)^6}^\infty [D_e(-\frac{r_e^6}{r_e^6})2x + (\frac{r_e^{12}}{r_e^{12}})x^2 - D_e(-2x + x^2)] \times \]

\[ \exp[-b(-2x + x^2)]x^{-3/2} \, dx/ \]

\[ \int_{(r_e/R)^6}^\infty \exp[-b(-2x + x^2)]x^{-3/2} \, dx . \]

Splitting the integral into its components leads to

\[ C_1 = \frac{\int_{(r_e/R)^6}^\infty (2x + (\frac{r_e^6}{r_e^6})x^2) \exp[-b(-2x + x^2)]x^{-3/2} \, dx}{\int_{(r_e/R)^6}^\infty \exp[-b(-2x + x^2)]x^{-3/2} \, dx} \]

\[ \frac{D_e \int_{(r_e/R)^6}^\infty (-2x + x^2) \exp[-b(-2x + x^2)]x^{-3/2} \, dx}{\int_{(r_e/R)^6}^\infty \exp[-b(2x + x^2)]x^{-3/2} \, dx} . \]

In evaluating the exponent a substitution is made:

\[ (x - 1)^2 = x^2 - 2x + 1 \quad \text{or} \quad -2x + x^2 = (x - 1)^2 - 1 \]

and
\[-b(-2x + x^2) = b - b(x - 1)^2\]

or

\[\exp[-b(-2x + x^2)] = \exp[b]\exp[-b(x - 1)^2].\]

The integrals now become

\[
C_1 = \left. \frac{\exp[b] \int_0^{\infty} \frac{-r_e^{1/6}}{r_e} (r_e/R)^6 (2x + \frac{r_e^{1/6}}{r_e} x^2) \exp[-b(x - 1)^2] x^{-3/2} \, dx}{\exp[b] \int_0^{\infty} \exp[-b(x - 1)^2] x^{-3/2} \, dx} \right. 
\]

\[
- \frac{\exp[b] \int_0^{\infty} (-2x + x^2) \exp[-b(x - 1)^2] x^{-3/2} \, dx}{\exp[b] \int_0^{\infty} \exp[-b(x - 1)^2] x^{-3/2} \, dx} 
\]

Gathering like powers of \(x\) leaves

\[
C_1 = \left. \frac{\int_0^{\infty} \exp[-b(x - 1)^2] x^{-1/2} \, dx}{\int_0^{\infty} \exp[-b(x - 1)^2] x^{-3/2} \, dx} \right. 
\]

\[
\frac{\int_0^{\infty} \exp[-b(x - 1)^2] x^{1/2} \, dx}{\int_0^{\infty} \exp[-b(x - 1)^2] x^{-3/2} \, dx} 
\]

Use of equation 19 gives the final expression
\[ C_1 = \frac{-\left(2[D_e - D_e', \frac{r_e^6}{r_e^6}]F_1(b, r_e/R) + [D_e - D_e', \frac{r_e^{12}}{r_e^{12}}]F_1(b, r_e/R)\right)}{F_3(b, r_e/R)}. \]

Similarly, for \( C_2 \)
\[ C_2 = \frac{\left(-1\right)^2}{2!} \int_0^R D^2(r) \exp\left[-\frac{U(r)}{kT}\right] r^2 \, dr \cdot \]
\[ \int_0^R \exp\left[-\frac{U(r)}{kT}\right] r^2 \, dr. \]
Again, using equation 12 and substituting \( \frac{r_e^6}{r_e} \) and \( r^2 \, dr = -\frac{1}{6} r_e^3 x^{-3/2} \, dx \) as before gives
\[ C_2 = \frac{1}{2} \int_0^{\infty} \left[D_e'^2 \frac{r_e^6}{r_e^6} (-x + r_e^6 \frac{x^2}{2r_e^6}) - 2D_e(-x + \frac{1}{2}x^2)\right]^2 x \]
\[ \exp\left[-2b(-x + \frac{1}{2}x^2)\right] x^{-3/2} \, dx. \]
\[ \int_0^{\infty} \exp\left[-2b(-x + \frac{1}{2}x^2)\right] x^{-3/2} \, dx. \]
Squaring the first term yields
\[ C_2 = \frac{1}{2} \int_0^{\infty} \left[4D_e'^2 \frac{r_e^{12}}{r_e^{12}} \left(x^2 - \frac{r_e^6}{r_e^6} x^3 + \frac{r_e^{12}}{4r_e^{12}} x^4\right) \right. \]
\[ - 8D_e'^2 D_e \frac{r_e^6}{r_e^6} \left(x^2 - \left(\frac{1}{2} + \frac{r_e^6}{2r_e^6}\right)x^3 + \frac{r_e^6}{4r_e^6} x^4\right) \]
\[ + 4D_e^2 \left(x^2 - x^3 + \frac{x^4}{4}\right) \exp\left[-2b(-x + \frac{1}{2}x^2)\right] x^{-3/2} \, dx. \]
\[ \int_0^{\infty} \exp\left[-2b(-x + \frac{1}{2}x^2)\right] x^{-3/2} \, dx. \]
Gathering like powers of $x$ gives

$$C_2 = \frac{1}{2} \int_{(r_e/R)^6} \left[ (4D_e \frac{r_e^{12}}{r_e^{12}} - 8D_e \frac{r_e^{6}}{r_e^{6}} + 4D_e^2) x^2 ight. \\
- (4D_e \frac{r_e^{18}}{r_e^{18}} - 4D_e \frac{r_e^{6}}{r_e^{6}} - 4D_e \frac{r_e^{12}}{r_e^{12}} + 4D_e^2) x^3 \\
+ \left. (D_e \frac{r_e^{24}}{r_e^{24}} - 2D_e \frac{r_e^{12}}{r_e^{12}} + D_e^2) x^4 \right] \exp[-2b(-x + \frac{1}{2}x^2)] x^{-3/2} dx / (r_e/R)^6 \\
- \frac{1}{2} \int_{(r_e/R)^6} \exp[-2b(-x + \frac{1}{2}x^2)] x^{-3/2} dx .$$

Again using

$$\exp[-2b(-x + \frac{1}{2}x^2)] = \exp[-b] \exp[-b(x - 1)^2]$$

and factoring gives

$$C_2 = \{2[D_e - D_e' \frac{r_e^{6}}{r_e^{6}}] \frac{r_e^{12}}{r_e^{12}} \int_{(r_e/R)^6} \exp[-b(x - 1)^2] x^{1/2} dx \\
- 2[D_e - D_e' \frac{r_e^{6}}{r_e^{6}}] [D_e - D_e' \frac{r_e^{12}}{r_e^{12}}] \int_{(r_e/R)^6} \exp[-b(x - 1)^2] x^{3/2} dx \\
+ \frac{1}{2} [D_e - D_e' \frac{r_e^{12}}{r_e^{12}}] \int_{(r_e/R)^6} \exp[-b(x - 1)^2] x^{5/2} dx / (r_e/R)^6 \\
- \frac{1}{2} \int_{(r_e/R)^6} \exp[-b(x - 1)^2] x^{-3/2} dx .$$
Finally, substitution of equation 19 gives the desired expression

\[ C_2 = \left\{ 2[D_e - D_e'] \frac{r_e^6}{r_e^6} \right\}^2 F_1(b, r_e/R) - 2[D_e - D_e'] \frac{r_e^6}{r_e^6} \left[ D_e - D_e' \frac{r_e^{12}}{r_e^{12}} \right] \times \]

\[ F_3(b, r_e/R) + \frac{1}{2} \left[ D_e - D_e' \frac{r_e^{12}}{r_e^{12}} \right]^2 F_5(b, r_e/R) \}/F_{-3}(b, r_e/R) . \]
Appendix D

This program evaluates coefficients A1 and A2 for pressure-eff Studies based on the Van der Waals model. It requires input of De, De', and Re' as well as pressure.

DEFINT I-N, DEFOG A-H, Q-2

DIM P(50), R(50), C(50), F(10), G(10), Y(50), P(50), A(5, 100), X(5, 100), AP(100), F(10), G(10), Y(50), P(50), A(5, 100)

PRINT "THE FOLLOWING DATA-INPUT REQUESTS ARE FOR A PARTICULAR DE AND A PARTICULAR RE AT A GIVEN TEMPERATURE." PRINT "AFTER ENTERING THESE DATA YOU WILL BE ASKED FOR DE' AND RE'. THE COEFFICIENTS WILL BE EVALUATED. YOU WILL THEN BE GIVEN THE OPPORTUNITY TO INPUT NEW DE AND/OR RE' FOR THE SAME GROUND-STATE VALUES." PRINT "WHEN READY TO BEGIN PRESS 'ENTER'".

CLS
PRINT "THE FOLLOWING INPUT REQUESTS CONCERN THE NC-3 INTEGRATION OF THE F S" PRINT "DEFAULT VALUE OF \( \gamma \): INPUT" PRINT "MAXIMUM ERROR PER SEGMENT (%): EM" PRINT "CONVERGENCE LIMIT AS % SEGMENT IS OF MAXIMUM SEGMENT";
CLS
INPUT "FOR HOW MANY PRESSURES DO YOU WISH TO EVALUATE COEFFICIENTS"; NQ PRINT "PRESSURE MUST BE IN UNITS OF METRIC BAR.";

FOR I=1 TO NQ: INPUT "PRESSURE = "; P(I): RL(I) = (9.8673*D3/P(I))^(1/3) NEXT I

FOR I=1 TO NQ: PRINT "PRESSURE = " P(I) " BAR, R = " RL(I) PRINT " THE LOWER LIMIT = " XY(I-1)

FOR I=1 TO 4: GOSUB 568 NEXT

CLC
CLS
PRINT "THE FOLLOWING F VALUES WERE EVALUATED FOR:" PRINT " T = " T " K" PRINT " DE = " D PRINT " RE = " R ANGSTROMS" PRINT"" PRINT"

CLS
CLS
PRINT "WHEN YOU WISH TO CONTINUE PRESS 'ENTER':";

IF BS="2" THEN 330
PRINT "THE COEFFICIENTS WILL NOW BE EVALUATED. WHEN YOU WISH TO CONTINUE PRESS 'ENTER':";

GOTO 410
CLS: PRINT "INPUT OF EXCITED-STATE PARAMETERS REQUESTED.  REMEMBER TO USE UNIT 5 OF "DE" AND "RE" AND ANGSTROMS FOR "RE"."
"INPUT "DE" =", DP: INPUT "RE" =", RP
50 AT=RP/RP: CT=DP-AT: DT=D-AT: AT=AT+AT
70 FOR I=1 TO N
90 CI:I=-2: DP*CT+F(I, 1)-DT*FI(2, 1): FI(0, I):
90 C2 : =-1: DP*CT+DT*FI(3, 1)-4: DP*CT+DT*FI(4, 1): FI(0, I+)
400 NEXT
410 IF Nu=63 THEN CMD "Z", "ON"
420 PRINT PRINT PRINT PRINT "THE COEFFICIENTS ARE PRINTED FOR THE FOLLOWING PARAMETER:
PRINT T = "T", K": PRINT DE = "D", "DE" PRINT RE = "R" ANGSTROMS": PRINT
DP: PRINT DP: PRINT DP: PRINT "DE" = "DE": PRINT DP: PRINT RE = "RE" ANGSTROMS": PRINT
430 NL=1: Nu=5
440 IF Nu=0 THEN Nu=0
450 IF Nu<63 THEN CMD "Z", "ON"
460 FOR I=NL TO Nu:PRINT "PRESSURE = "P(I)" BAR"
470 PRINT A1 = "C1(I)" "D$": PRINT A2 = "C2(I)" "D$": "D$": "D$
480 NEXT
490 CMD "Z", "OFF"
500 INPUT "WHEN YOU WISH TO CONTINUE PRESS 'ENTER'": C$ 510 IF Nu=0 THEN GOTO 530
520 NL=NL+5: Nu=NL+5: GOTO 540
530 INPUT "DO YOU WISH TO CALCULATE VALUES FOR DATA ANALYSIS (Y/N)": A$: IF A$="Y" THEN GOSUB 1290
540 CLS: INPUT "DO YOU WISH TO EVALUATE OR INPUT COEFFICIENTS FOR NEW EXCITED-STATE VALUES BUT SAME GROUND-STATE VALUES": C$
550 IF C$="YES" GOTO 525
551 INPUT "DO YOU WISH TO INPUT A NEW RE FOR THE SAME DE (Y/N)": A$: IF A$="Y" THEN GO TO 1290 560 END
568 IF Nu<>0 THEN GOTO 1080
569 IF W=1 THEN 572: ELSE IF T$="NO" THEN 575
570 INPUT "DO YOU WANT TO INPUT A VALUE FOR B": T$: IF T$="NO" THEN 575
571 INPUT "INPUT A VALUE FOR B": B
572 N=2+LQ-3: NW=0: Nu=NQ-1: CLS: PRINT "CURRENTLY CALCULATING F("N")": W=1: IF LQ>0 THEN 630
573 GOTO 630
575 NW=0: Nu=0: N=2+LQ-3: NQ=NQ-1: CLS: PRINT "CURRENTLY CALCULATING F("N")": IF LQ>0 THEN 690
590 IF DE="CM-1" THEN B=D/6.959979-1/T: GOTO 630: ELSE GOTO 590
590 IF DE="CM-1" THEN B=D/6.959979-1/T: GOTO 600
600 IF DE="EV" THEN B=D/6.1747-5/T: GOTO 600: ELSE GOTO 600
610 IF DE="EV" THEN B=D/6.1747-5/T: GOTO 600: ELSE GOTO 620
620 INPUT "UNITS GIVEN FOR DE NOT RECOGNIZABLE. SHOULD BE CM-1, CM-1, EV OR EV. INPUT VALUE OF B, BUT BE CAREFUL; WHATEVER UNITS YOU HAVE USED FOR DE, THE SAME MUST BE USED FOR "DE"": B
630 FOR I=TONN: XT=XY(I): IT=1: PT=P(I+1): RT=RL(I+1)
640 FOR K=ITONN: IF XY(K)<XT THEN XT=XY(K): IT=K: PT=P(K+1): RT=RL(K+1)
650 NEXT
660 XY(IT)=XY(I): XY(I)=XT: P(I+1)=P(I+1): P(I+1)=PT: RL(IT+1)=RL(I+1): RL(I+1)=RT
670 NEXT
680 REM *****CYCLE IS INITIATED******
690 XI=XU
700 XI(XQ, 0)=XI: M=0: AM=0. DQ: AT=0. DQ
710 IF LW=1 THEN 590
720 Y=X(XQ, M)=1. DQ
730 IF Y*X(LQ, M)>0.5-2 THEN 750
740 Nu=Nu+1: M=NU+10: HT=QD+2. I: NU: GOTO 950
750 F(0)=1: F(1)=2: 0=8*Y
760 F(2)=2: 0=8*4: 0=8*Y(2): F(3)=12: 0=8*8*2-8: 0=8*Y*B(3)
770 F(4)=12: 0=8*2-8: 0=8*Y*B(2): B=16: 0=8*Y*B(1)
780 F(5)=120: 0=8*8*2-8: 0=8*Y*B(1): B=16: 0=8*Y*B(1)
IF NW=62 THEN CMD"Z", "ON"
1215 KG=1 INPUT"DO YOU WISH TO PRINT MATRIX ELEMENTS ON PRINTER <Y/N>". A$ IF A$="N" THEN CMD"Z","OFF". KG=0
1220 PRINT"" PRINT"THE MATRIX ELEMENTS ASSOCIATED WITH A1 ARE PRINTED"
1230 NL=1: NU=2
1240 IF NG:NU THEN NU=NG
1250 FOR I=NL: NTONU: PRINT"PRESSURE = "P(I)" BAR"
1260 IF NG=1 THEN GOTO 1400
1270 IF NW=63 AND KG=1 THEN CMD"Z", "OFF"
1280 PRINT"WHEN READY TO CONTINUE PRESS ENTER";
A$ IF A$="N" THEN CMD"Z", "OFF"
1290 NEXTI
1300 NL=NL+2: NU=NU+3: IF NW=63 AND KG=1 THEN CMD"Z", "ON"
1310 GOTO 1400
1320 INPUT"DO YOU WISH TO HAVE DETERMINANT VALUES PRINTED ON PRINTER <Y/N>". A$ IF A$="N" THEN KG=0 ELSE KG=1
1330 NV=0. IF NW=63 AND KG=1 THEN CMD"Z", "ON"
1340 FOR I=1: NTONG-2
1350 FOR J=I+1: NTONG
1360 FOR K=I+1: NTONG
1370 DT=P(I,1)+P(J,2)+P(K,3)+P(I,2)+P(K,1)+P(I,3)+P(J,2)+P(K,1)
1380 PRINT"FOR THE SET "I", J", K", "PRINT" DT LB=NV/3 LC=LB*3: IF LC=NV THEN CMD"D", "OFF"
1390 INPUT"WHEN READY TO CONTINUE PRESS ENTER";
A$ IF A$="N" THEN KG=0 ELSE KG=1
1400 INPUT"DO YOU WISH TO HAVE DETERMINANT VALUES PRINTED ON PRINTER <Y/N>". A$ IF A$="N" THEN KG=0 ELSE KG=1
1410 NV=0. IF NW=63 AND KG=1 THEN CMD"Z", "ON"
1420 FOR I=1: NTONG-2
1430 FOR J=I+1: NTONG
1440 FOR K=I+1: NTONG
1450 DT=P(I,1)+P(J,2)+P(K,3)+P(I,2)+P(K,1)
1460 PRINT"CALCULATED FROM P("I") AND P("J"): PRINT" DE' = "DC" D$:PRINT" DE = "DC ANGSTROMS"
1470 INPUT"WHEN READY TO CONTINUE PRESS ENTER";
A$ IF NW=63 AND KG=1 THEN CMD"Z", "ON"
1480 NEXTK
1490 NEXTJ
1500 NEXT
1510 NEXTI
1520 FOR I=1: NTONG-1
1530 FOR J=1: NTONG
1540 P(I)=P(I,1)+P(J,1)
1550 IF NW=63 AND KG=1 THEN CMD"Z", "OFF"
1560 PRINT"CALCULATED FROM P("I") AND P("J"): PRINT" DE' = "DC" D$:PRINT" DE = "DC ANGSTROMS"
1570 INPUT"WHEN READY TO CONTINUE PRESS ENTER";
A$ IF NW=63 AND KG=1 THEN CMD"Z", "OFF"
1580 CMD"Z", "OFF": INPUT"WHEN READY TO CONTINUE PRESS ENTER";
A$ IF IFNW=63 THEN CMD"Z", "ON"
1590 NEXTK
1600 NEXTI
1610 IF NW=62 THEN CMD"Z", "ON"
1620 IF NW=63 THEN IFNU=NU3
1630 NEXTI
1640 IF NW=63 THEN CMD"Z", "ON"
1650 IF NW=63 THEN CMD"Z", "ON"
1660 IF NW=63 THEN CMD"Z", "ON"
1670 IF NW=63 THEN CMD"Z", "ON"
1680 IF NW=63 THEN CMD"Z", "ON"
1690 IF NW=63 THEN CMD"Z", "ON"
1700 IF NW=63 THEN CMD"Z", "ON"
1710 IF NW=63 THEN CMD"Z", "ON"
1720 RETURN
1730 FOR I=1 TO NO
1740 PRINT"FOR P="P(I)"
"BAR"
1741 INPUT" A1=":C1(I):INPUT" A2=":C2(I)
1750 NEXT
1760 RETURN
Appendix E

In an attempt to determine the variation of the excited state intermolecular parameters associated with an error in the estimate of the ground state, a hypothetical system was constructed and analyzed by the same means as the experimental systems. A ground state of $r_e = 6 \, \text{Å}$ and $D_e = 200 \, \text{cm}^{-1}$ was used in conjunction with an excited state of $r_e' = 5.5 \, \text{Å}$ and $D_e' = 300 \, \text{cm}^{-1}$. These values represent the "exact" intermolecular parameters of the system.

Coefficients were calculated at 0.5, 1, 2, 3, 4, 5, 6, 8, 10 and 15 bar. These coefficients were then used to calculate new excited state intermolecular parameters as the ground state $r_e$ and $D_e$ values were systematically varied. The new excited state values could then be compared to the original parameters of $r_e' = 5.5 \, \text{Å}$ and $D_e' = 300 \, \text{cm}^{-1}$, permitting an estimate of the variation in the excited state caused by utilizing "incorrect" ground state values (Table 8).

Experimentally the determinants should fluctuate (see p. 52) about zero, with approximately equal numbers of positive and negative values. The absolute value of the determinant is expected to be small since theoretically all determinants are zero. Therefore, the magnitudes of the determinants serve as indicators of the accuracy of ground state and/or coefficient values.

In the CH$_3$I/SF$_6$ systems analyzed, determinant values averaged in the tens of thousands. One set showed a preponderance of negative values but the other sets were evenly split. For thiirane perturbed with SF$_6$ the determinants were smaller. Determinants of a few thousand,
Table 8

<table>
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<th>( r_e (\text{Å}) )</th>
<th>( D_e (\text{cm}^{-1}) )</th>
<th>( r'_e (\text{Å}) )</th>
<th>( D'_e (\text{cm}^{-1}) )</th>
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<tr>
<td>5.95</td>
<td>225</td>
<td>5.50</td>
<td>321</td>
</tr>
<tr>
<td>6.05</td>
<td>175</td>
<td>5.49</td>
<td>279</td>
</tr>
<tr>
<td>6.05</td>
<td>225</td>
<td>5.60</td>
<td>317</td>
</tr>
<tr>
<td><strong>6.00</strong></td>
<td>200</td>
<td>5.51</td>
<td>303</td>
</tr>
</tbody>
</table>

**Note:** Coefficients varied \((C_1 + 5, C_2 + 10)\)

and even into the hundreds, were not uncommon when DBH was used to estimate the ground state parameters. However, these values rose to the low tens of thousands when the ground state estimate was based on comparison with oxirane used. Thiirane with SF\(_6\) gave the smallest determinant values of any system analyzed. Determinants were negative, then positive, and towards the end fluctuated to both positive and negative numbers.

The determinants for thiirane with both argon and tetrafluoro-methane were larger, with many values in the hundreds of thousands. For thiirane with argon determinant values were mostly negative, whereas for thiirane with CF\(_4\) the majority of the determinants were positive.

For the hypothetical system the determinants were relatively small, with values usually in the hundreds. Determinants were smallest when only one parameter was varied. Interestingly, when the coefficients...
were varied versus the ground state parameters, determinants became much larger with values in the tens and even hundreds of thousands. This indicates a much greater sensitivity to the coefficients than ground state values.

It also was found that if one or both of the ground state parameters was overestimated (value increased) virtually all determinants were positive, while if parameters were underestimated determinants were negative. Finally, when one parameter was overestimated and the other underestimated the sign of the determinants predominantly followed the change in direction of the potential well depth.

In addition it was found that errors in the potential well depth were always minimum at the lower pressures while errors in the intermolecular distance were minimum at the higher pressures. This seems to indicate a method by which both ground state and excited state estimates could be improved. A program could be written to calculate new ground state parameters based on the input of the coefficients and excited state values. \(D_e\)' from the low pressure and \(r_e\)' from the high pressure (with the excited state errors minimized) should give a better estimate of the ground state parameters than what was used originally. The process would be repeated until consistent values of the excited state parameters could be calculated at all pressures. Thus, the errors in \(r_e\), \(D_e\), \(r_e\)' and \(D_e\)' would all be minimized.


