

May 1973

# Resonant Raman Scattering from Iodine: Spectral Changes with Excitation Frequency

P. F. Williams

*University of Nebraska - Lincoln, pfw@moi.unl.edu*

D. L. Rousseau

*Bell Laboratories, Murray Hill, New Jersey*

Follow this and additional works at: <http://digitalcommons.unl.edu/elecengwilliams>



Part of the [Electrical and Computer Engineering Commons](#)

---

Williams, P. F. and Rousseau, D. L., "Resonant Raman Scattering from Iodine: Spectral Changes with Excitation Frequency" (1973). *P. F. (Paul Frazer) Williams Publications*. 31.

<http://digitalcommons.unl.edu/elecengwilliams/31>

This Article is brought to you for free and open access by the Electrical & Computer Engineering, Department of at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in P. F. (Paul Frazer) Williams Publications by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.

helpful discussions and to Mr. F. Alkemade and Mr. K. Sherwin for their technical assistance. We also thank Mr. R. McNaughton for the loan of equipment.

\*Work supported by the National Science Foundation under Grant No. GP-28415.

†Permanent address: Laboratoire de Spectroscopie Hertzienne de l'École Normale Supérieure, Paris, France.

<sup>1</sup>See, for example, A. Corney and G. W. Series, *Proc. Phys. Soc.* **83**, 207 (1964). For a simple calculation of quantum beat signals see also P. Franken, *Phys. Rev.* **121**, 508 (1961), Appendix I.

<sup>2</sup>J. N. Dodd, R. D. Kaul, and D. M. Warrington, *Proc. Phys. Soc., London* **84**, 176 (1964); E. B. Alexandrov, *Opt. Spektrosk.* **17**, 957 (1964) [*Opt. Spectrosc.* **17**, 522 (1964)]; J. N. Dodd, W. J. Sandle, and D. Zissermann, *Proc. Phys. Soc., London* **92**, 497 (1967).

<sup>3</sup>T. Hadeishi and W. A. Nierenberg, *Phys. Rev. Lett.* **14**, 891 (1965).

<sup>4</sup>See, for example, H. J. Andrä, *Phys. Rev. Lett.* **25**, 325 (1970); H. G. Berg and J. L. Subtil, *Phys. Rev. Lett.* **27**, 1103 (1971).

<sup>5</sup>K. Tillman, H. J. Andrä, and W. Wittman, *Phys. Rev. Lett.* **30**, 155 (1973).

<sup>6</sup>T. W. Hänsch, *Appl. Opt.* **11**, 895 (1972).

<sup>7</sup>W. Gornik, D. Kaiser, W. Lange, J. Luther, and H. H. Schulz, *Opt. Commun.* **6**, 327 (1972).

<sup>8</sup>A related phenomenon, modulations in the wings of level-crossing signals under dye laser pulsed-light excitation, has been recently reported. P. Schenck, R. C. Hilborn, and H. Metcalf, *Bull. Amer. Phys. Soc.* **18**, 121 (1973).

<sup>9</sup>S. Svanberg and S. Rydberg, *Z. Phys.* **227**, 216 (1969), and references therein.

<sup>10</sup>Slightly different values for  $1/\Gamma$  are obtained by various authors. See, for example, Ref. 8.

<sup>11</sup>J. Brossel and F. Bitter, *Phys. Rev.* **86**, 308 (1952).

<sup>12</sup>F. D. Colegrove, P. A. Franken, R. R. Lewis, and R. H. Sands, *Phys. Rev. Lett.* **3**, 420 (1959).

<sup>13</sup>See, for example, T. W. Hänsch, I. S. Shahin, and A. L. Schawlow, *Phys. Rev. Lett.* **27**, 707 (1971), and references therein.

## Resonant Raman Scattering from Iodine: Spectral Changes with Excitation Frequency

P. F. Williams and D. L. Rousseau

*Bell Laboratories, Murray Hill, New Jersey 07974*

(Received 12 March 1973)

We have recorded high-resolution resonant Raman spectra of molecular iodine which show very pronounced systematic spectral band-shape variations with incident laser frequency. This frequency dependence and the presence of the multiple overtones in resonant Raman scattering from iodine may be explained by a theory in which the scattering intensity depends on Franck-Condon overlap integrals. We have obtained semi-quantitative agreement between the observed spectra and spectra calculated from this theory.

Reports of previous Raman studies on molecular iodine have discussed light scattering below<sup>1</sup> and above<sup>2,3</sup> the  $B(^3\Pi_{0^+u})$ -state dissociation limit ( $20162\text{ cm}^{-1}$ ). Resonant Raman scattering above the dissociation limit<sup>2,3</sup> is characterized by several overtones, each exhibiting a complex structure. The details of this structure were attributed to  $O$ ,  $Q$ , and  $S$  ground-electronic-state  $X(^1\Sigma_{0^+g})$  vibrational-rotational branches of several thermally populated hot bands.<sup>3</sup> Although it has been shown<sup>3</sup> that frequencies of the discrete features of the spectra result from bandheads of  $S$  and  $Q$  branches (the  $O$  branch results only in broad structureless scattering<sup>3</sup>), no explanation has been given for the relative intensities of these features. Furthermore, prior investigations of scattering above the  $B$ -state dissociation limit

have reported only on spectra obtained with  $4880\text{-}\text{\AA}$  excitation and no mention was made of structural changes occurring with different laser frequencies. In this Letter we wish to report very marked changes in the spectrum as a function of the incident laser frequency above the  $B$ -state dissociation limit. We attribute these changes to a variation in the magnitude of the Franck-Condon overlap integral and discuss a theory from which we have calculated spectra. This calculation both explains the occurrence of the multiple overtones in resonant Raman scattering from molecular iodine and accounts for the structural changes with incident laser frequency.

The Raman data reported here were obtained in a standard manner. The gaseous iodine in a sample cell was held at a pressure of about 25

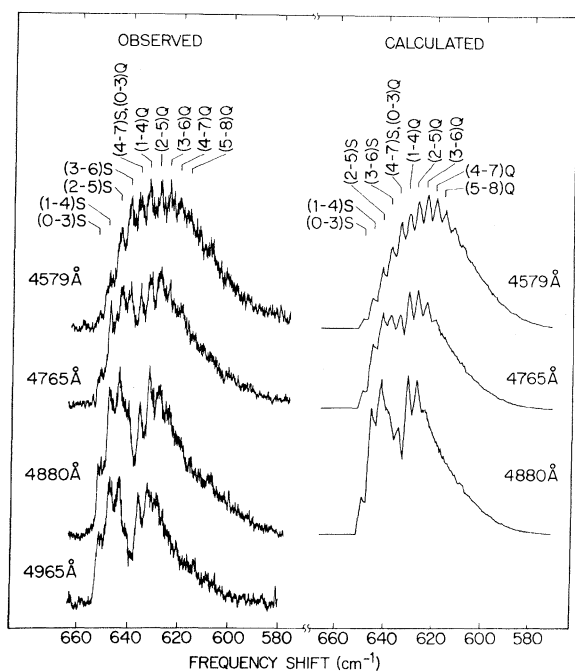


FIG. 1. Experimentally observed and theoretically calculated iodine resonant Raman spectra for the  $\Delta v'' = 3$  transition. S and Q numbers refer to the initial- and final-vibrational-state assignments of the S and Q branches.

mm and a temperature of about 420°K. Spectra were obtained at excitation wavelengths of 4965, 4880, 4765, and 4579 Å. The laser power level was held constant at 500 mW. From the relative intensities of the rotational lines of  $N_2$ , which was added to one sample cell, the iodine temperature due to heating in the laser beam was determined to be 520–620°K depending on the excitation frequency.

Iodine resonant Raman spectra are shown for  $\Delta v'' = 3$  (the second overtone) in Fig. 1, and for  $\Delta v'' = 8$  (the seventh overtone) in Fig. 2.<sup>4</sup> The variation of the structural features of these spectra, with different laser frequencies, is very pronounced. In spectra of the second overtone in Fig. 1 for the 4965- and the 4880-Å excitations, there is a clear distinction between the S- and Q-branch envelopes. This distinction has disappeared in the 4579-Å spectrum. This behavior results from the tendency of higher hot bands to become more prominent with higher laser frequency. At excitation frequencies just above the dissociation limit, the spectra are dominated by transitions originating from the  $v'' = 0, 1, 2$  vibrational levels of the ground electronic state. However, at high laser frequencies Raman transi-

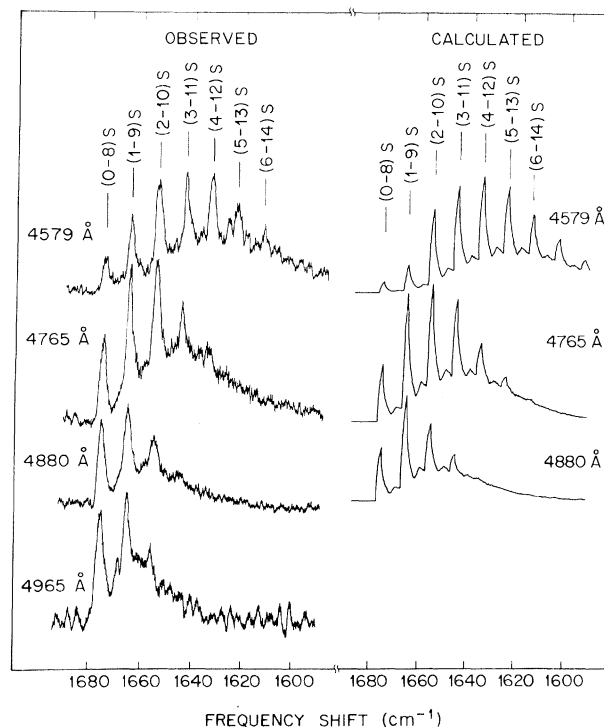


FIG. 2. Experimentally observed and theoretically calculated iodine resonant Raman spectra for the  $\Delta v'' = 8$  transition. S numbers refer to the initial- and final-vibrational-state assignments of the S branches.

tions originating from the higher-energy vibrational levels ( $v'' > 2$ ) become increasingly important. This behavior is better exemplified in the seventh-overtone spectra in Fig. 2. Here, the dominant contributions are from S-branch transitions. In the spectrum obtained at 4965 Å only the  $v'' = 0 \rightarrow v'' = 8$  and the  $v'' = 1 \rightarrow v'' = 9$  transitions are large. Transitions originating from higher vibrational levels can hardly be seen. In contrast, in the spectrum obtained with the 4579-Å laser line, transitions as high as  $v'' = 6 \rightarrow v'' = 14$  may readily be seen, and the strongest lines in the spectrum originate from  $v'' = 2 \rightarrow v'' = 10$ ,  $v'' = 3 \rightarrow v'' = 11$ , and  $v'' = 4 \rightarrow v'' = 12$  transitions. A similar trend was observed for the other overtones.

Scattering from the Raman transition  $|i\rangle \rightarrow |f\rangle$  is customarily treated in second-order perturbation theory<sup>5,6</sup> where a component  $\alpha$  of the polarizability tensor may be expressed as

$$\alpha \propto \sum_e \left( \frac{M_{fe} M_{ei}}{\omega_{ei} - \omega_0} + \frac{M_{fe} M_{ei}}{\omega_{ef} + \omega_0} \right). \quad (1)$$

Here  $\omega_0$  is the excitation frequency and the  $M$ 's

are total transition amplitudes between the intermediate state ( $e$ ) and the initial ( $i$ ) and final ( $f$ ) states. Near resonance, the second term in Eq. (1) is much smaller than the first and will be neglected for the remainder of the discussion. Application of the Born-Oppenheimer approximation and the Herzberg-Teller expansion<sup>5</sup> separates the matrix elements  $M$  into an electronic part and a vibrational part. The lowest-order term of Eq. (1) then becomes

$$\alpha \propto \sum_e \sum_{v_e'} \frac{M_{ge}' M_{eg}' \langle v_f'' | v_e'' \rangle \langle v_e' | v_i'' \rangle}{\omega_{v_e'} - \omega_0}, \quad (2)$$

where  $M'$  is now an electronic matrix element only, and the terms  $\langle v_i'' | v_e' \rangle$  and  $\langle v_e' | v_i'' \rangle$  are Franck-Condon overlap integrals between ground- and excited-electronic-state vibrational levels. The next higher-order terms are of the form

$$\alpha \propto \sum_e \sum_{v_e'} \sum_k h_{ek} \frac{M_{ge}' M_{gk}' \langle v_f'' | v_e' \rangle \langle v_e' | Q | v_i'' \rangle}{(\omega_{v_e'} - \omega_0)(\omega_k - \omega_e)}, \quad (3)$$

where  $k$  designates an excited electronic state other than  $e$ ,  $h_{ek}$  is a perturbation energy resulting from the mixing of excited electronic states, and  $Q$  is the internuclear normal coordinate.<sup>6,7</sup>

As pointed out by Albrecht,<sup>8</sup> in vibrational Raman scattering far from resonance the energy denominator in Eq. (2) is nearly constant, so this term vanishes because of completeness, and the Raman intensity is derived from Eq. (3). However, with the excitation frequency well into resonance, as is the case in our experiments, in no approximation is the denominator in Eq. (2) a constant, so the lowest-order term does not vanish and, in fact, is expected to be the dominant term.<sup>8</sup>

To interpret the major features of the iodine resonance Raman spectrum, we have evaluated  $\alpha$  in Eq. (2) for the continuum  $B$ -state wave functions above the  $B$ -state dissociation limit. The interatomic potential curves were determined by interpolating between turning points reported from Rydberg-Klein-Rees calculations by Zare<sup>9</sup> and Verma<sup>10</sup> for the  $X(^1\Sigma_0^+g)$  state, and by Tellinghuisen<sup>11</sup> for the  $B(^3\Pi_{0+u})$  state. The potential curve at small internuclear distances above the  $B$ -state dissociation limit was obtained by extrapolating from the turning-point curve with an  $a+b/r^{12}$  function.

To evaluate  $\alpha$  for the  $B$  continuum states, the summation over  $v_e'$  in Eq. (2) may be replaced by an integral. The singularity in the integral may be handled in the usual way<sup>12</sup>:

$$\alpha \propto |M_{eg}'|^2 \left[ P \int_0^\infty \langle v_f'' | v_e' \rangle \langle v_e' | v_i'' \rangle \rho(\omega_{v_e'}) (\omega_{v_e'} - \omega_0)^{-1} d\omega_{v_e'} - i\pi \langle v_f'' | v_e' \rangle \langle v_e' | v_i'' \rangle \rho(\omega_{v_e'}) \Big|_{\omega_{v_e'} = \omega_0} \right], \quad (4)$$

where  $|v_e'\rangle$  is the continuum state with energy  $\omega_{v_e'}$ , and  $\rho(\omega_{v_e'})$  is the density of continuum vibrational states. The continuum wave functions for the  $B$  state and the discrete wave functions of the ground state were calculated numerically by the Numerov method,<sup>9,13</sup> and the overlap integrals then were evaluated, also numerically.  $\alpha$  was determined separately for each value of  $J$ . To avoid recalculating the wave functions for each  $J$  value, the  $J$  dependence of the Franck-Condon factors was approximated by shifting the  $J=0$  electronic potential functions by the appropriate rotational energy.

By introducing the vibrational and rotational population factors, and the rotational-branch intensity factors as given by Placzek and Teller,<sup>14</sup> we calculated the intensity of a given vibrational-rotational transition.<sup>15</sup> A spectral intensity distribution was then determined by calculating the  $O$ -,  $Q$ -, and  $S$ -branch Raman intensities for each of the vibrational-rotational Raman frequencies obtained from the latest spectroscopic data.<sup>16</sup> All the rotational levels with significant popula-

tion (up to  $J=400$ ), and hot bands originating from the  $v''=0-9$  ground-electronic-state vibrational levels were included in the calculation for each overtone. The calculated spectra were produced by convoluting the spectral intensity with a two-wave-number rectangular slit function.

Calculated spectra for the second and seventh overtones are shown in Figs. 1 and 2, respectively. Since the 4965-Å excitation line is less than 100  $\text{cm}^{-1}$  above the dissociation limit, a spectrum for this wavelength was not calculated since contributions to the scattering from the discrete states are expected to be large for this excitation line. The frequencies of the dominant features in the calculated spectra agree with those in the observed spectra within experimental error. The absolute intensity of the calculated spectrum for each laser line was scaled to the experimental intensity. Except for this scale factor, these spectra were calculated with no adjustable parameters.

In the calculated spectra, as in the observed

spectra, the trend toward the dominance of higher hot bands at higher laser frequencies may be seen. This results from changes in the magnitude of the Franck-Condon factors with incident laser frequency. In all the calculated spectra there is a general weakness of transitions originating from the lowest vibrational states (i.e.,  $v''=0,1$ ) as compared with the observed spectra. We believe this discrepancy results from our approximation that the spectral features are completely governed by the  $B$  continuum states. We have neglected contributions to the sum in Eq. (2) from the  ${}^1\Pi_{1u}$  repulsive state and from the discrete levels of the  $B$  state.

The ratio of the intensity of the second to seventh overtone was measured for each laser excitation frequency, and a calculated ratio was also obtained. For spectra taken at 4579 and 4765 Å the calculated and measured intensity ratios agreed within experimental error (~10%). However, at 4880 Å the ratios differed by about 50%. Again we believe this difference at 4880 Å results from including only the  $B$  continuum states in our intermediate-state calculation. We have not measured the relative intensities of a given overtone with laser frequency because variations in the absorption coefficient over the range of interest and also the thermal-lens effect complicate the experimental measurement.

It is expected that the discrete states may make contributions to the scattering intensities especially for laser wavelengths near the dissociation limit. In addition, recent photodissociation<sup>17</sup> and optical-absorption<sup>11</sup> experiments have indicated that the  ${}^1\Pi_{1u}$  repulsive state has a non-negligible oscillator strength in the part of the spectrum we are investigating, and would therefore also make a contribution to the Raman scattering intensity. However, the position of this repulsive state is not well known. Preliminary calculations of resonant Raman spectra including this state give the same general trends as the spectra calculated from the  $B$  state only. When trying to obtain a quantitative agreement between the observed and calculated spectra, we have found that the calculated spectrum is extremely sensitive to the position of this potential function. After including the contribution of the discrete states to the scattering in Eq. (2), it should be possible to determine the position of this repulsive potential accurately from resonant-Raman-scattering data in this frequency region. Other techniques lack com-

parable sensitivity.

<sup>1</sup>D. G. Fouche and D. K. Chang, *Phys. Rev. Lett.* **29**, 536 (1972); R. L. St. Peters, S. D. Silverstein, M. Lapp, and P. M. Penney, *Phys. Rev. Lett.* **30**, 191 (1973); M. Berjot, M. Jacon, and L. Bernard, *Can. J. Spectrosc.* **17**, 60 (1972).

<sup>2</sup>W. Holzer, W. F. Murphy, and H. J. Bernstein, *J. Chem. Phys.* **52**, 399, 469 (1970).

<sup>3</sup>W. Kieffer and H. J. Bernstein, *J. Mol. Spectrosc.* **43**, 366 (1972).

<sup>4</sup>The minor differences between the spectra reported here and those reported in Ref. 3 probably result from the lower sample temperatures in our experiments.

<sup>5</sup>J. Tang and A. C. Albrecht, in *Raman Spectroscopy*, edited by H. A. Szymanski (Plenum, New York, 1970), Vol. 2, Chap. 2.

<sup>6</sup>A. C. Albrecht, *J. Chem. Phys.* **34**, 1476 (1961).

<sup>7</sup>A complete discussion of this theory of Raman intensities is given in Refs. 5 and 6.

<sup>8</sup>Theories to explain the resonant Raman scattering of iodine have been proposed by M. Berjot, M. Jacon, and L. Bernard [*Opt. Commun.* **4**, 246 (1971)], and by L. A. Nafie, P. Stein, and W. L. Peticolas [*Chem. Phys. Lett.* **12**, 131 (1971)]. Berjot, Jacon, and Bernard applied a qualitatively similar approach as that discussed here to explain the relative intensity of the iodine fundamental vibration as a function of laser frequency. However, they included only transitions from  $v''=0$  and 1 in their calculations. The spectra reported here clearly demonstrate the necessity of including transitions from higher vibrational levels to describe these resonant Raman processes properly. Nafie, Stein, and Peticolas proposed that the overtone intensity may be explained by calculating harmonic-oscillator transitions from a third- and higher-order perturbation theory and have neglected the second-order term [our Eq. (2)]. However, because of the variation in the energy denominator, the quantum-mechanical sum rule [J. H. Van Vleck, *Proc. Nat. Acad. Sci. U. S.* **15**, 754 (1929)] is not applicable, so the second-order term does not vanish. Nafie, Stein, and Peticolas's treatment is not appropriate to describe resonant Raman scattering from iodine.

<sup>9</sup>R. N. Zare, *J. Chem. Phys.* **40**, 1934 (1964).

<sup>10</sup>R. D. Verma, *J. Chem. Phys.* **32**, 738 (1960).

<sup>11</sup>J. Tellinghuisen, to be published.

<sup>12</sup>H. Bethe and E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic, New York, 1957), p. 41.

<sup>13</sup>J. W. Cooley, *Math. Computation* **15**, 363 (1961).

<sup>14</sup>G. Placzek and E. Teller, *Z. Phys.* **81**, 209 (1933).

<sup>15</sup>G. Placzek, *Handbuch der Radiologie* (Akademische Verlagsgesellschaft, Leipzig, 1934), Vol. 2, Chap. 21.

<sup>16</sup>R. J. LeRoy, *J. Chem. Phys.* **52**, 2683 (1970).

<sup>17</sup>R. J. Oldman, R. K. Sander, and K. R. Wilson, *J. Chem. Phys.* **54**, 4127 (1971).