eter dependence and the steep increase with bombarding energy.

In summary, we have demonstrated the importance of multistep processes in the quasimolecular description of heavy-ion inner-shell excitations. The nonadiabacity of the electronic motion is the origin of violent coupling between neighboring states which have the effect of increasing the excitation rates. The number of vacancies depends monotonically [Eq. (8)] on the number of initially occupied states. To obtain accurate results for vacancy formation (and thus also for positron production) the initial distribution of electrons (i.e., the position of the Fermi surface) must be known. The characteristics of the excitation process are changed slightly by multistep excitation, leading to a weaker dependence on impact parameter and energy. Detailed studies of the impact-parameter, energy, and charge dependence of inner-shell excitation as a function of the binding energies and coupling strengths entering the coupled-channels calculations will be necessary for the envisaged spectroscopy of superheavy quasimolecules.

This work was supported by the Bundesministerium für Forschung und Technologie and by the Gesellschaft für Schwerionenforschung.

[1]W. Betz, G. Soff, B. Müller, and W. Greiner, Phys. Rev. Lett. 37, 1046 (1976).

[2]J. S. Greenberg, H. Bokemeyer, H. Emling, E. Grosse, D. Schwalm, and F. Bosch, Phys. Rev. Lett. 39, 1404 (1977).

[3]D. Liesen, P. Armbruster, H.-H. Behnke, and S. Hagmann, Z. Phys. A 288, 417 (1978).

[4]J. R. Macdonald, P. Armbruster, H. H. Behncke, F. Folkmann, S. Hagmann, D. Liesen, P. H. Mokler, and A. Warczak, Z. Phys. A 284, 57 (1978).

[5]H.-H. Behncke, D. Liesen, S. Hagmann, P. H. Mokler, and P. Armbruster, Z. Phys. A 288, 35 (1978).

[6]R. Anholt and W. E. Meyerhof, Phys. Lett. 64A, 381 (1978).

[7]T. H. Rihan, B. Müller, and W. Greiner, J. Phys. B 12, 761 (1979).

[8]A. L. Reading, Phys. Rev. A 8, 3262 (1973).

[9]J. F. Ford and A. L. Reading, to be published.

[10]J. Reinhardt, B. Müller, and W. Greiner, in *Proceedings of the International Workshop on Coherence and Correlation in Atomic Collisions*, edited by H. Kleinpoppen and J. F. Williams (Plenum, New York, 1979).

[11]G. Soff, W. Betz, J. Reinhardt, and J. Rafelski, Phys. Scr. 17, 417 (1978).

[12]G. Soff, W. Greiner, W. Betz, and B. Müller, Phys. Rev. A 20, 169 (1979).

[13]G. Soff, W. Betz, B. Müller, W. Greiner, and E. Merzbacher, Phys.Lett. 65A, 19 (1978); B. Müller, G. Soff, W. Greiner, and V. Ceausescu, Z. Phys. A 285, 27 (1978).

[14]R. Anholt, W. E. Meyerhof and Ch. Stoller, Z. Phys. A 291, 1287 (1979).

[15]D. Liesen, private communication.

[16]P. A. Amundsen, J. Phys. B 11, L737 (1978).

Observations on the $v=0 \rightarrow v=5$ Rotational-Vibrational Band of HD

F. W. Dalby[a] and J. Vigué

Laboratoire de Spectroscopie Hertzienne de l'Ecole Normale Supérieure, Université Pierre et Marie Curie, 75230 Paris Cédex 05, France, and Department of Physics, University of British Columbia, Vancouver, British Columbia V6T 1W5, Canada

(Received 21 August 1979)

The $v=0 \rightarrow v=5$ rotational-vibrational spectrum of free HD has been observed by means of photoacoustic spectroscopy. The electric dipole matrix elements are found to depend significantly upon the rotational quantum number. The dependence of the frequency of the $R(1)$ line upon density has been determined.

Electric dipole vibrational spectra of free H_2 molecules are rigorously forbidden by symmetry. For HD, electric-dipole spectra are permitted by symmetry but are very weak, being allowed only because of nonadiabatic effects. They are forbidden within the Born-Oppenheimer approximation. The first observation of a HD dipole vibrational spectrum was made by Herzberg.[1] Trefler and Gush[2] have studied the pure rotational spectrum. McKellar, Goetz, and Ramsay[3] have reported wavelength and intensity measurements of the stronger lines in the 3-0, 4-0, 5-0, and 6-0 HD bands (we denote $v=0 \rightarrow v_f \neq 0$ by v_f-0 hereafter) and surveyed earlier work. The spectral properties of HD are of astronomical importance as the vibrational spectrum of HD has been

observed from the atmosphere of Jupiter by Trauger, Roesler, and Carleton, and Traub.[4]

In all the experiments described above, a very long absorption path length and a rather large quantity of HD were required. For studies of the 5-0 band McKellar, Goetz, and Ramsay[3] used a 30.3-m multiple-traversal cell to obtain absorption paths of 3 km and require about 500 liters of gas. Here we report on experiments on the 5-0 band of HD in a cell of volume 1.2 cm^3 and of path length 4.0 cm which give well-developed spectra at high signal to noise. The technique used here, photoacoustic spectroscopy, although first reported by Alexander Graham Bell[5] and actively pursued since the advent of lasers, particularly for the analysis of weak infrared spectra, presents some novel features.

Rosengren[6] has discussed the optimal optoacoustic detector design and reviewed earlier work. The best performance in photoacoustic spectroscopy of which we are aware claims a 10^{-9} cm^{-1} to 10^{-10} cm^{-1} limit of detection (Patel and Kerl[7]). Another very sensitive result is that of Koch and Lahmann,[8] who claim a limit of detection of 1.0×10^{-9} cm^{-1} with a 1-mW laser source. Bragg and Hayden-Smith[9] briefly report photoacoustic observation of the $R(0)$, $R(1)$, and $R(2)$ lines of the 5-0 band of HD.

In our experiments the photoacoustic cell is placed within the laser cavity of a Coherent Inc. (model 499) dye laser pumped by a Spectra Physics (model 165) argon-ion laser. The cell is made of stainless steel and contains a 4.0-cm length absorption path of 0.4-cm radius. Midway along the cell a capacitor microphone of $\frac{1}{4}$ inch radius is mounted perpendicularly to the absorption axis. The net active volume of the cell is 1.2 cm^3. The windows of the cell are made of well-polished Spectrosil mounted at the Brewster angle. The pump laser is square-wave intensity modulated at a frequency in the range 10–500 Hz. The detector is a Brüel and Kjaer capacitor microphone No. 4133, modified so as to be vacuum tight, feeding a No. 2619 preamplifier. The microphone has a response of 12.5 mV/Pa, constant to better than ± 2 dB over a frequency range 5 Hz to 40×10^3 Hz, and a noise figure of 2 μV/Hz near 50 Hz.

Absorption of light produces a pressure signal at the laser modulation frequency which is detected by means of the microphone feeding into a phase-sensitive detector. All our work was done with a 1 second integration time. The laser frequency was scanned either by rotation of a Lyot filter giving a laser-frequency full width at half maximum of 1.2 cm^{-1} or, for more limited regions, by rotating a 1-mm polished quartz plate which gives a full width at half maximum of $\simeq 0.12$ cm^{-1}. The dye-laser output mirror had 4% transmission for the higher-resolution experiments. For these experiments typical argon-ion laser power was 3.5 W, producing 300-mW dye-laser output and 15 W in the cavity. For the longer scans at lower resolution, a nominally 100% reflecting dye-laser output mirror was used giving a cavity power somewhat greater than 15 W.

We have observed a continuous photoacoustic signal throughout the Rhodamine-6G spectral region which is from 10–100 times as strong as the strongest observed HD line. Hence the sharp HD lines are observed upon a pedestal. The continuous signal, presumably due to absorption near the inner surfaces of the quartz windows, has been discussed by Rosengren.[6] Small fluctuations in laser intensity produce fluctuations in the pedestal and constitute the principal source of noise in our experiment and limit our detectability to about 10^{-8} cm^{-1}. Preliminary attempts to decrease the effects of the pedestal by frequency modulation of the laser and by the use of sapphire windows whose thermal conductivity is significantly higher than that of quartz were unseccessful. However, both of these procedures, as well as lengthening of the cell, should ultimately significantly reduce the magnitude of the pedestal.

Figure 1 shows the low-resolution spectrum observed from a sample of HD of better than 98% purity at 1.5 amagats density. The laser modulation frequency was 60 Hz (note that the mains frequency in Paris is 50 Hz!) The relative intensities of the Hd lines did not vary significantly when the density varied from 0.5 to 4.0 amagats or when the modulation frequency varied from 10 to 100 Hz.

The strengths of the observed HD lines depend linearly upon the optical absorption coefficients, the quantities of primary interest here, and are proportional to $f(J) = \beta(1 + \omega^2 T_r^2)^{-1/2}$, where ω is the angular modulation frequency, T_r the effective vibrational-translational relaxation time and β the fraction of energy transferred to translational energy (see Rosengren[6]). We find experimentally that there is no significant J dependence due to the relaxation process and $f(J)$ can be taken to be independent of J. More precisely, if we assume $f(J) = A + BJ^2$, then for HD at 1.5 amagats, 294 °K, and $\omega = 2\pi \times 60$ rad/s, we find that $|B/A| < 0.01$. This conclusion on the lack of

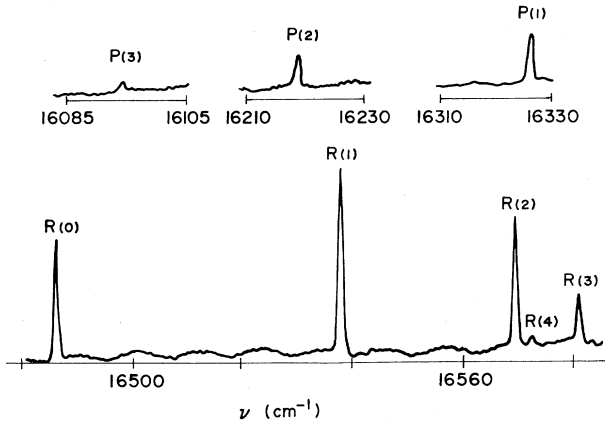

FIG. 1. The photoacoustic spectrum of the 5-0 band of HD. The HD density is 1.5 amagat.

significant J dependence in the vibrational-translational relaxation follows for other reasonable assumptions about possible functional forms of $f(J)$. From observation of the phase and intensity of the photoacoustic signal as a function of modulation frequency ω we find $T_r < 5\times10^{-3}$ s for the same density and pressure conditions. The $v=1$ to $v=0$ H_2-H_2 vibrational relaxation rate at room temperature and 1.0 amagat density has been measured by Audibert, Joffrin, and Ducuing,[10] who find $T_r = 0.38\times10^{-3}$ s.

We can therefore use the intensity of the observed photoacoustic lines to determine relative electric-dipole absorption strengths. From our observed relative intensities and the absolute value of the integrated absorption coefficient for the $R(1)$ line determined by McKellar, Goetz, and Ramsay,[3] we can determine the electric-dipole transition-matrix element for the various P and R lines from the expression

$$\mu^2 = \frac{3hc}{8\pi^3 N_0}\,\frac{2J+1}{\nu n P_J}\,\alpha,$$

where N_0 is 2.687×10^{19} molecules/cm^3, $n=+J$ for the $P(J)$ line and $n=J+1$ for the $R(J)$ line, P_J is the fraction of molecules in the Jth rotational state, ν the frequency of the transition in cm^{-1}, and α the absorption coefficient in cm^{-2} amagat^{-1}. The derived matrix elements plotted against m, where $m=-J$ for the $P(J)$ lines and $m=J+1$ for the $R(J)$ line, are shown in Fig. 2. The strong m dependence which arises from the mixing of electronic Π states due to the interaction $-2B\vec{J}\cdot\vec{L}$ has been discussed by Bunker.[11]

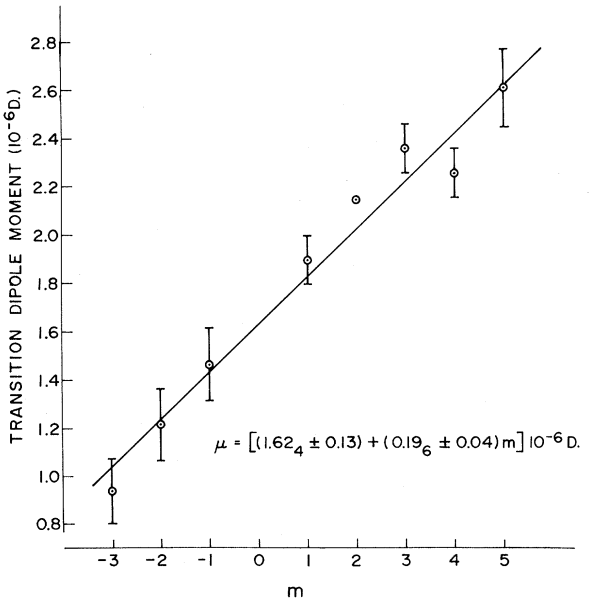

FIG. 2. Variation of the HD transition dipole moment with m, where $m=-J$ for the $P(J)$ lines and $m=J+1$ for the $R(J)$ lines.

We find experimentally that

$$\mu_{0\text{-}5} = [(1.62_4 \pm 0.13) + (0.19_6 \pm 0.04)m]\times10^{-6}\ \text{D}.$$

Further numerical work will have to be done in order to achieve a quantitative comparison with Bunker's theory.

The weakest HD line we have observed, the $P(3)$ line, has for a density of 1.5 amagats an integrated absorption coefficient of 10.5×10^{-9} cm^{-2}, and a peak absorption coefficient of 6.6×10^{-8} cm^{-1}. Since the laser linewidth is about 1.2 cm^{-1} and the HD linewidth is 0.15 cm^{-1}, this sensitivity is equivalent to observation at an absorption coefficient of 8×10^{-9} cm^{-1}.

We have made a few observations on the $R(1)$ line at higher resolution. With the 1-mm quartz plate in the cavity, the laser linewidth is reduced to about 0.1 cm^{-1} and contains just a few longitudinal modes. Although this resolution for a study of the HD line shapes, since the Doppler width of the lines is 0.12 cm^{-1}, we can make accurate determination of frequency and reasonably accurate measurements of linewidths.

The spectra are calibrated by simultaneous observation of absorption of molecular iodine and the photoacoustic absorption in HD. We have used the atlas of Gerstenkorn and Luc[12] for the identification and frequencies of the I_2 lines. Note that all the frequencies listed there must be re-

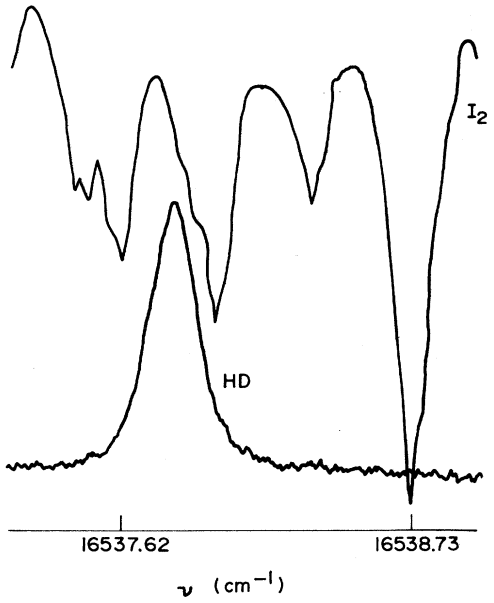

FIG. 3. Higher-resolution spectrum of the $R(1)$ line. The HD density is 4.0 amagats. The molecular iodine absorption spectrum for a path length of 20 cm and a room-temperature vapor pressure is used for calibration. The frequencies of the I_2 lines are 0.0056 cm^{-1} too high.

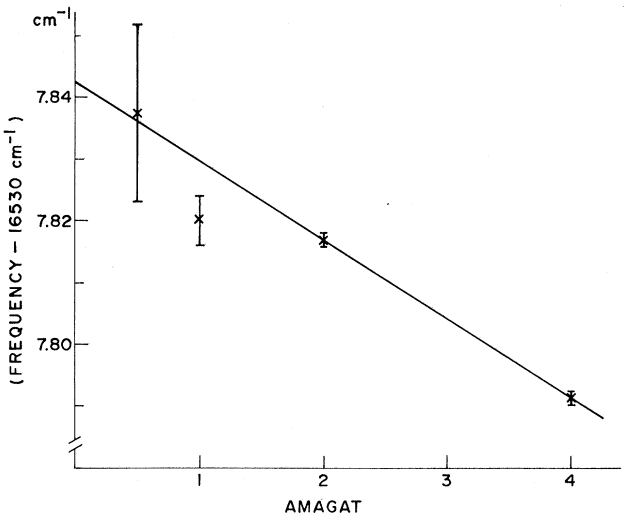

FIG. 4. The frequency of the $R(1)$ line as a function of density. These frequencies are relative to I_2 values, which are 0.0056 cm^{-1} too high.

duced by 0.0056 cm^{-1}.

Figure 3 shows an example of the spectrum observed at 4.0 amagats. In Fig. 4 we plot the observed frequency against density for the $R(1)$ line. The principal limitation on the accuracy of our measurements are due to mode changes in the laser and not in the signal to noise of the HD line —even at 0.5 amagat. From this plot we find the frequency of the $R(1)$ line in inverse centimeters as a function of the HD density in amagat, ρ, to be

$$\nu = (16\,537.836_8 \pm 0.003) - (0.012_8 \pm 0.001)\rho\,.$$

The result is in good agreement with McKellar, Goetz, and Ramsay,[3] who find a frequency of 16 537.816 cm^{-1} for a pressure of $\simeq 1$ atm at 295 K and a density shift of $\simeq -0.01$ cm^{-1} $amagat^{-1}$.

The linewidth of the $R(1)$ line can be estimated from the deconvolution of the observed linewidths. We find the full width at half maximum to be 0.16 $\pm$ 0.02 cm^{-1} throughout the range 0.5 to 4.0 amagats HD. The width is somewhat greater than the calculated Doppler width, 0.12 cm^{-1}, but within the accuracy of our present observations is largely independent of pressure.

It is clear that this work could be significantly extended, as both our laser and our photoacoustic cell were and could be greatly improved. We hope to study in some detail the HD line shapes, observe much weaker HD and H_2 spectra, and elucidate the relaxation mechanism. It is also tempting to imagine the possibility of Doppler-free spectroscopy upon a transition whose natural linewidth is less than 10^{-3} Hz!

We wish to thank Professor Ducuing for the loan of the HD sample, and Monsieur Mallet for his excellent work on the cell. One of us (F.W.D.) thanks Professor Lehmann, Professor Cagnac, and their colleagues who made his stay (1977–1978) in Paris both profitable and enjoyable. We are grateful to Dr. R. A. Nodwell, Dr. M. H. L. Pryce, and Dr. C. Tai for helpful discussions.

[a]Present and permanent address: Department of Physics, University of British Columbia, Vancouver, B. C. V6T 1W5, Canada.

[1]G. Herzberg, Nature 166, 563 (1950).

[2]M. Trefler and H. P. Gush, Phys. Rev. Lett. 20, 703 (1968).

[3]A. R. W. McKellar, W. Goetz, and D. A. Ramsay, Astrophys. J. 207, 663 (1976).

[4]J. T. Trauger, E. L. Roesler, N. P. Carleton, and W. A. Traub, Astrophys. Lett. 184, L137 (1973).

[5]A. G. Bell, Proc. Am. Assoc. Adv. Sci. 29, 115 (1880).

[6]L. Rosengren, Appl. Opt. 14, 1960 (1975).

[7]C. J. N. Patel and R. J. Kerl, Appl. Phys. Lett. 30, 578 (1977).

[8]K. P. Koch and W. Lahmann, Appl. Phys. Lett. 32,

289 (1978).
[9]S. Bragg and W. Hayden-Smith, Bull. Am. Astron. Soc. 9, 516 (1977).
[10]M. M. Audibert, C. Joffrin, and J. Ducuing, Chem. Phys. Lett. 19, 26 (1973).
[11]P. R. Bunker, J. Mol. Spectoros. 46, 119 (1973).
[12]S. Gersterkorn and P. Luc. Atlas du Spectre d'Absorption de la Molécule de l'Iode (Centre National de la Recherche Scientifique, Paris, France, to be published), and Rev. Phys. Appl. 14, 791 (1979).

Propagation Effect in Resonance Fluorescence: Spatial Antibunching of Photons

Martine Le Berre-Rousseau
Laboratoire des Signaux et Systèmes, 91190, Gif-sur-Yvette, France

and

E. Ressayre and A. Tallet
Laboratoire de Photophysique Moléculaire, Université Paris-Sud, 91405 Orsay, France
(Received 15 June 1979)

We investigate spatial fluctuations of the cooperative emission of radiation by a two-level-atom system driven by a resonant electric field. For very small absorption length, a directional photon antibunching effect is expected.

Experiments of propagation of intense light pulses in near-resonant gaseous media exhibit spatial fluctuations of the scattered light in the limit of very large atomic densities. These fluctuations are visible on a screen located at the exit and relatively far from the source within a finite spatial extension, more precisely in a ring centered on the propagation axis of the electric field.[1,2]

Two different processes take part in the emission of radiation by a medium of N_c two-level atoms per cm^3. One is the isotropic and incoherent emission of fluorescence, the intensity of which is the sum of the atomic intensities and then is proportional to N_c. The other is the cooperative emission, the intensity of which is proportional to N_c^2 and spatially focused in a small solid angle about the propagation axis. At the space-time point $(\vec{R},t)$ far from the source, these intensities are given by the expectation values of

$$I_{\text{incoh}}(\vec{R},t)=\frac{1}{R^2}\sum_k R_k^{+}(t-|\vec{R}-\vec{x}_k|/c)R_k^{-}(t-|\vec{R}-\vec{x}_k|/c) \tag{1}$$

for the incoherent emission and of

$$I_{\text{coop}}(\vec{R},t)=\frac{1}{R^2}\sum_{k\neq l}\sum_l R_k^{+}(t-|\vec{R}-\vec{x}_k|/c)R_l^{-}(t-|\vec{R}-\vec{x}_l|/c) \tag{2}$$

for the cooperative emission, where $\vec{x}_k$ is the position of atom with label k in the sample and $R_k^{\pm}(t)$ are the raising and lowering operators associated with it, expressed in the Heisenberg picture,

$$R_k^{\pm}=|\pm\rangle\langle\mp|\,. \tag{3}$$

The correlation function of the full intensity, at equal time t and at two observation points $\vec{R}_1$ and $\vec{R}_2$, displays the spatial fluctuations which may be visible on a screen to the naked eye. It is the sum of three relevant terms: The first two terms display the correlations in the intensity of the incoherent emission; they exhibit an isotropic structure. The last term displays the correlations in the intensity of the cooperative emission and is the relevant part of the full correlation function in the small solid angle in which the cooperative emission takes place.

The first one describes the well-known bunching effect.[3,4] For spatial fluctuations it is proportional