Laboratory Observations of Collision-Induced Emission in the Fundamental Vibration-Rotation Band of H_2

R. Krech, G. Caledonia, and S. Schertzer
Physical Sciences Inc., Research Park, Andover, Massachusetts 01810

and

K. Ritter, T. Wilkerson, and L. Cotnoir
Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742

and

R. Taylor
CVD Inc., Woburn, Massachusetts 01801

and

G. Birnbaum
National Bureau of Standards, Washington, D.C. 20234

(Received 21 October 1982)

Laboratory experiments on collision-induced emission are reported. The light source is hydrogen-argon mixtures, shock heated to temperatures up to 2850 K and densities up to 49 amagats in a shock tube. For the fundamental vibration-rotation band of H_2, absolute intensity, band strength and shape, and the dependence on temperature and density have been determined.

PACS numbers: 33.20.Ea, 34.50.Ez

This paper reports the first laboratory observations of collision-induced emission (CIE), the inverse process of the collision-induced absorption (CIA) that has already been well characterized[1] for a number of gases at and below room temperature. Collision-induced (or "pressure-induced") processes give rise to optical spectra for molecules that, by virtue of their symmetry, do not have an electric dipole moment in the electronic ground state. Such collisional processes can make significant contributions to radiative transfer in gases. For example, CIA by H_2 is the dominant source of infrared opacity in stellar atmospheres[2] and CIE by H_2 has been found to be an important source of infrared radiation in planetary atmospheres.[3-5] Van Kranendonk and co-workers[6,7] developed the theory for collision-induced absorption in H_2, assuming that a collision between two H_2 molecules induces a transient dipole in them due to both their permanent quadrupole moments and the overlap of the molecular electron clouds. The induced dipole, modulated by internal molecular motions, gives rise to vibrational, rotational, and translational transitions. At elevated temperatures, line structure in the bands is obliterated, establishing broad, continuous emission bands in the near, middle, and far infrared.

The present measurements on the fundamental collision-induced H_2 vibration band at 2.4 μm were undertaken to verify that CIE could be studied quantitatively under controlled, high-temperature conditions. A shock tube[8] is used to heat H_2:Ar mixtures to temperatures of 1000–3000 K and densities in the range 10–49 amagats. The test time near the end of the shock tube behind the reflected shock wave is ~1 ms for steady gas conditions in thermal equilibrium. A high-speed scanning spectrometer[9] records the spectra of infrared emission from the shock tube, sweeping over the range 2.1–2.7 μm in 300 μs. For the fundamental vibration-rotation band of H_2, we have determined absolute emission intensity, band strength and shape, and the dependence on temperature and density.

The shock tube was chosen for this work because it rapidly heats and compresses a large volume of gas that equilibrates quickly ($t < 1$ μs) to steady, thermal conditions. Temperature, pressure, and density are readily calculated from the shock-wave velocity *via* the Rankine-Hugoniot conservation equations for fluid mass, momentum, and energy.[8] In prior experiments the agreement of temperature, density, atomic and molecular excitation, etc., with shock-wave calculations has been noted.[10] Possible discrepancies due to viscosity and heat conduction are minimized by operating at the high gas densities used in the present work. Lastly, the simultaneously elevated temperatures and densities attainable with a shock tube greatly exceed those available with other devices. Thus, the high densities needed to manifest collision-induced spectra could be obtained while elevating the temperature enough to examine high-temperature effects.

The ultimate objective of this work is to use high temperatures to bring out particularly the overlap contributions to collision-induced phenomena. By studying the temperature dependence of the spectral moments (e.g., see Futrelle[11]) or from quantum calculations of line shape (e.g., see Birnbaum *et al.*[12]) it will be possible to investigate important aspects of the intermolecular potential. Although the parameters in the model for the induced dipole produced by overlap forces have been established for H_2 from measurements at and below room temperature,[1,7,13,14] similar parameters for elevated temperature have not been determined. Since collision-induced emission is sensitive to the repulsive region, the temperature dependence of the line shape and spectral moments at high temperatures should be sensitive to the overlap mechanisms. The H_2/rare-gas systems offer an especially attractive opportunity for observing this, since induction is strongly influenced by the overlap interaction.

The gases and thermal conditions used in our work have been carefully chosen to minimize complications such as dipole-allowed radiation by atomic hydrogen and argon, or by H_2O as an impurity, and hydrogen dissociation that could lead to H-atom collisional effects on H_2. However, not all of the relevant physical phenomena could be anticipated by the prior theoretical treatment, as is discussed below, and further work is planned on the theory as well as the measurements.

The emission measurements are conducted behind reflected shocks in a 16.2-cm-i.d. stainless-steel shock tube. The driver and test sections are 3 and 6 m long, respectively. The pressure is measured directly with a piezoelectric pressure transducer located at the optical port. Temperature is calculated from the shock velocity, which is measured from the time of arrival of the incident shock wave at successive pressure-transducer stations located at 50 cm intervals in the test section.

Test gases have been either mixtures of 10% or 20% H_2 in argon, or pure argon to determine the background emission levels. Primary standard-grade gas mixtures were obtained from Linde and used without further purification. Water-vapor impurity levels are stated to be <3 ppm. Before each test, the shock tube is evacuated with a diffusion pump to $\sim 10^{-8}$ atm to minimize contamination from outgassing. No water band emission was expected or observed in these experiments.

Optical measurements are made through 25.4×6 mm^2 sapphire windows located 5 cm from the end wall. Two detection systems are used in each experiment. The integrated band intensity is measured with a narrow-band radiometer, consisting of an InSb detector and a 2.1 to 2.7 μm band-pass filter. Spectrally resolved measurements are obtained with a 0.5-m Ebert synchronized high-speed scanning spectrometer. The instrument was built at Avco Everett Research Laboratory, Inc. for high-temperature plasma measurements.[9] At present the instrument is equipped with a 10-line/mm grating blazed at 3 μm. The detector is a 2.5×5 mm InSb detector with a 1.5-μm-long pass filter (blocking $>10^{-3}$ to uv). A resolution of 0.1 μm is obtained with 0.5-mm slits, and a spectral range of about 1.5 μm is scanned during a typical test time (>1 ms). Before each measurement the absolute sensitivity of each detector is measured with a 1200-K blackbody. The spectrometer is flushed with dry N_2 to eliminate atmospheric absorption. All instrumentation is interfaced with a computer-controlled CAMAC data-acquisition system containing two 10-bit, four-channel LeCroy digitizers. The calibrations and the raw spectrum, recorded as intensity versus time, are stored in the computer and then converted into plots of intensity or emissivity versus wavelength.

The data are displayed as spectral emissivity, which is the ratio of the observed intensity to that of a blackbody at the same temperature. A typical spectrum of the Q branch of the H_2 vibration-rotation band at 2.4 μm is shown in Fig. 1. Total gas density is 27.3 amagats at 1572 K (157.2 atm). It is anticipated from both room-temperature observations and theoretical predictions[2,6,7] that the observed emission is primarily due to the H_2-Ar interaction with a small contribution from the H_2-H_2 interaction. The spectrum is superimposed over a relatively flat background emission observed in measurements performed in pure argon under similar conditions (see Fig. 1). The origin of this latter emission is not known.

All eighteen of our observed CIE spectra of H_2 in argon have this appearance, featuring a strong broad emission band centered near 2.4 μm. Peak

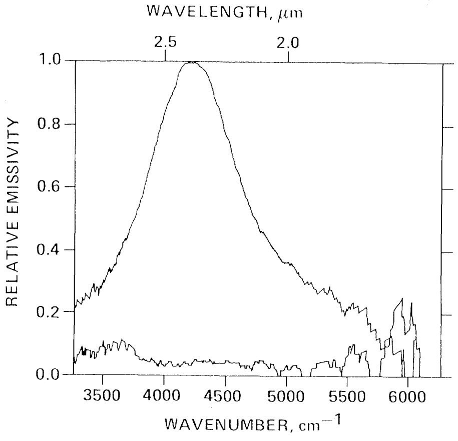

FIG. 1. Normalized spectral emissivity vs wave number, $\epsilon_{peak} = 0.071$. Upper trace: (20% H_2)/(80% Ar), $T = 1570$ K, $\rho = 27.3$ amagats. Lower trace: 100% Ar, $T = 1540$ K, $\rho = 32.5$ amagats.

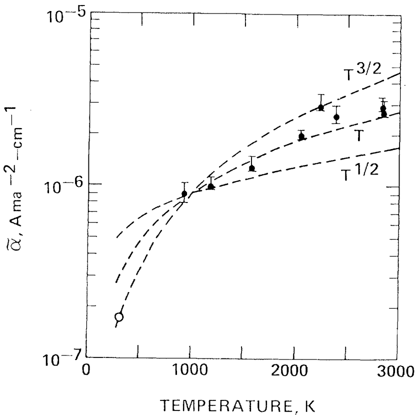

FIG. 2. Reduced band strength for the fundamental vibration-rotation band of H_2 [specific to (20% H_2)/(80% Ar)]. Temperature dependences have been arbitrarily normalized at $T = 1000$ K.

emissivities are at least a factor of 20 greater than the out-of-band H_2-Ar background, or the in-band pure-argon background. The emission intensity was found to vary as the square of the gas density, thus confirming that the radiation mechanism is indeed collision-induced emission. To our knowledge, this is the first observation of CIE under controlled laboratory conditions.

The measurements were performed over the temperature range of 1000–3000 K. In all cases the Q branch was by far the dominant band feature. The spectral data have been integrated so as to specify the reduced band strength $\tilde{\alpha}$ defined as

$$\tilde{\alpha} = \int k_\nu \, d\nu / \bar{\nu},$$

where ν is the wave number, $\bar{\nu}$ is the position of the band center, and k_ν is the absorption coefficient which is proportional to the spectral emissivity. (The spectral emissivity, ϵ_ν, is directly proportional to k_ν, if the gas is optically thin; i.e., $\epsilon < 0.1$.) The resulting reduced band strengths, specific to (20% H_2)/(80% Ar) mixtures, are shown in Fig. 2 and compared with a room-temperature measurement taken from Welsh's review.[1] Background emission was subtracted from the data, by using similar measurements performed in pure Ar, prior to the evaluation of the above integrals. In a few instances the long-wavelength portion of the band extended beyond the spectral range of the scan. The flags about the data points of Fig. 2 represent our best estimates of the uncertainties introduced by these background and cutoff effects.

The absolute emission was also checked in several cases with the integrating radiometer. The energy falling within the radiometer bandwidth agreed to within 25% with the equivalent spectrally resolved data. Moreover the radiometer showed that the infrared emission was constant during the shock-tube test time, indicating steady gas conditions.

As a further check on the absolute intensity accuracy, we made three measurements of the emission in the CO first overtone band[15-17] at 2.3 μm, for dilute CO-Ar mixtures over the temperature range 1170–2460 K, using the same apparatus. The intensities agreed to better than 40% with previous data[15] and theoretical predictions.[16,17]

Our data are specific to H_2-Ar collisions, for which no theoretical predictions are available. However, the following limited comparisons with theory have been attempted by using H_2-H_2 and H_2-He CIE predictions[2]: (1) The observed peak of the emission band occurs at 2.4 μm in accord with the spectroscopic parameters corresponding to the Q branch of H_2. (2) The observed band shape is approximately symmetrical, in contrast to Linsky's calculation[2] which shows enhanced intensity on the high-frequency side in accord with detailed balance. The shape we observe may be due to contributions from the H_2 transition $v = 2 \rightarrow v = 1$ (whose frequency is 236 cm^{-1} less than that for $v = 1 \rightarrow v = 0$), the relative intensity of the former increasing rapidly with temperature. This anharmonicity effect is common in vibration-rotation bands at high temperature, and was not considered in the theory[2] for H_2-H_2 and H_2-He. (3) The full width at half maximum of the H_2-Ar CIE band is typically ~0.5 μm, in general agreement[2] with theory, and scales approximately as $T^{1/2}$ which is similar to Linsky's predictions. (4) As indicated in Fig. 2, one cannot reconcile our integrated intensities with an *ad hoc* combination of Hare and Welsh's room-temperature[18] data for H_2-Ar plus Linsky's theoretical temperature scaling for H_2-H_2 and H_2-He (approximately $T^{1/2}$). This type of scaling clearly falls below our data and well outside any experimental uncertainties. Taken by themselves, our integrated emissivities vary as T^n, where $1 < n < \frac{3}{2}$.

The existing calculations, developed for room-temperature observations, may not be appropriate for the prediction of CIE at elevated temperatures. Certainly the important part of the intermolecular potential is more deeply probed at the high molecular velocities studied in this work, and the high vibrational temperatures provide significant radiation contributions from vibrational levels greater than $v = 1$.

The high-temperature CIE experiments may be readily extended to other collision partners and radiating molecules in order to provide a broad and accurate base for comparison with theory. A wider spectral range will be examined to gauge the potential contribution from the pure rotational bands of H_2 at longer wavelength, and implications of the band shapes will be investigated.

The direct observation of CIE band strengths at high temperature provides much more reliable values for emissivity than evidently can be computed theoretically at present. One can speculate that these bands will be found to play a greater role in high-temperature radiative transfer than expected heretofore. The contribution of excited states to collision-induced processes is important to assess both theoretically and experimentally. The work reported here demonstrates the feasibility of quantitative collision-induced emission experiments.

---

[1] H. L. Welsh, *International Reviews of Science, Physical Chemistry, Vol. 3: Spectroscopy* (Butterworths, London, 1972), Chap. 2, pp. 33–71.

[2] J. L. Linsky, Astrophys. J. 156, 989 (1969).

[3] D. Goorvitch and R. H. Tipping, J. Quant. Spectrosc. Radiat. Transfer 27, 399 (1982).

[4] R. Hanel, B. Conrath, M. Flasar, V. Kunde, P. Lowman, W. Maguire, J. Pearl, J. Pirraglia, R. Samuelson, D. Gauter, P. Gierasch, S. Kumar, and C. Ponnamperuma, Science 204, 972 (1979).

[5] V. Fine and H. Larson, Astrophys. J. 233, 1021 (1979).

[6] J. Van Kranendonk, Physica (Utrecht) 23, 825 (1957), and 24, 347 (1958), and Can. J. Phys. 46, 1173 (1968).

[7] J. Van Kranendonk and Z. J. Kiss, Can. J. Phys. 37, 1187 (1959).

[8] E. F. Green and J. P. Toennies, *Chemical Reactions in Shock Waves* (Arnold, London, 1964).

[9] J. C. Camm, R. L. Taylor, and R. Lynch, Appl. Opt. 6, 885 (1967).

[10] R. B. Bengtson, M. H. Miller, D. W. Koopman, and T. D. Wilkerson, Phys. Rev. A 3, 16 (1971).

[11] R. P. Futrelle, Phys. Rev. Lett. 19, 479 (1967).

[12] G. Birnbaum, Shih-I. Chu, A. Dalgarno, L. Frommhold, and E. L. Wright, "Theory of Collision-Induced Translation-Rotation Spectra: H_2–He" (to be published).

[13] D. R. Bosomworth and H. P. Gush, Can. J. Phys. 43, 751 (1965).

[14] J. L. Hunt and J. D. Poll, Can. J. Phys. 56, 950 (1978).

[15] J. C. Breeze and C. C. Ferriso, J. Chem. Phys. 43, 3253 (1965).

[16] L. A. Young and W. J. Eachus, J. Chem. Phys. 44, 4195 (1966).

[17] K. Kirby-Docken and B. Lui, J. Chem. Phys. 66, 4309 (1977).

[18] W. F. J. Hare and H. L. Welsh, Can. J. Phys. 36, 88 (1958).