



FIG. 2. Total reactive cross section ( $10^{-16} \text{ cm}^2$ ) vs relative kinetic energy (eV) for the  $\text{H} + \text{D}_2$  reaction. The open circles are from classical trajectory calculations (Refs. 9–11). The rectangles are the experimental results. The widths are the rms uncertainty in the relative kinetic energy due to the thermal motion of  $\text{D}_2$  in the bulb. The heights are the rms deviations of the results which are mainly caused by the instabilities in both lasers.

Molecular beam photodissociation experiments<sup>5</sup> show that 89.5% and 94.5% of the SH radicals are produced in the  $v = 0$  state by 193 and 248 nm light, respectively. LIF studies<sup>6</sup> show that these  $v = 0$  SH radicals are rotationally cold. Given these small fractions of slower H atoms (those which recoil from SH radicals with  $v > 0$ ) and that the slower H atoms still react although more slowly, it seems reasonable at this initial stage to neglect the systematic error caused by the slower H atoms. HI molecules were not used as H atom

sources in this LIF experiment because, surprisingly, they fluoresce when excited by Lyman  $\alpha$  radiation.

The wavelengths 248 and 193 nm produce H atoms from  $\text{H}_2\text{S}$  whose average translational energies relative to room temperature  $\text{D}_2$  are 0.84 and 1.95 eV, respectively. The corresponding measured values of the rate constants are  $1.42 \pm 0.14$  and  $3.65 \pm 0.20 \times 10^{-10} \text{ cm}^3/\text{molecule s}$ . Dividing these rate constants by the corresponding relative speeds yields the cross sections of  $0.99 \pm 0.11$  and  $1.68 \pm 0.12 \text{ Å}^2$ . The quoted error is the rms deviation of four measurements at the lower and five measurements at the higher energy.

Classical trajectory calculations have been carried out for the  $\text{H} + \text{D}_2$  system at a series of energies up to 1.95 eV.<sup>9–11</sup> These theoretical cross sections and the two experimental values are plotted in Fig. 2. The observed cross sections appear to be somewhat larger than the theoretical ones. The central question now is whether a fully quantal calculation would give a substantially different result from the classical one.

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## The far infrared spectrum of magnesium hydride

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In recent years, the magnesium hydride molecule has received growing attention as an astrophysically important species. Its occurrence in the sun<sup>1</sup> and other stars is well known through observation of its  $A^2\Pi-X^2\Sigma$  transition,<sup>2</sup> but

its existence in the interstellar medium has not been established. Magnesium, as well as sodium, calcium, and iron, has been postulated<sup>3</sup> to play an important role in the maintenance of charge balance in interstellar clouds through the

TABLE I. Observed transitions of  $^{24}\text{MgH}$  ( $X^2\Sigma^+$ ).

$N''$	$J''$	$F''$	$N'$	$J'$	$F'$	$\nu_{\text{obs}}$ (MHz)	$\nu_{\text{calc}}$ (MHz)	CO <sub>2</sub> lasing lines
2	2.5	3	3	2.5	3	1 028 202.5(10)	1 028 201.6	IR(36) <sup>12</sup> C <sup>16</sup> O <sub>2</sub> -IP(12) <sup>12</sup> C <sup>16</sup> O <sub>2</sub>
2	2.5	2	3	2.5	2	1 028 514.2(10)	1 028 513.7	IP(32) <sup>12</sup> C <sup>16</sup> O <sub>2</sub> -IP(18) <sup>13</sup> C <sup>16</sup> O <sub>2</sub>
2	2.5	2	3	3.5	3			
2	2.5	3	3	3.5	4	1 031 104.29(21) <sup>a</sup>	1 031 103.9	IIP(20) <sup>13</sup> C <sup>16</sup> O <sub>2</sub> - IR(6) <sup>12</sup> C <sup>16</sup> O <sub>2</sub>
3	3.5	4	4	3.5	4	1 369 797.0(10)	1 369 797.9	IR(34) <sup>12</sup> C <sup>16</sup> O <sub>2</sub> -IP(26) <sup>12</sup> C <sup>16</sup> O <sub>2</sub>
3	3.5	3	4	3.5	3	1 370 107.5(10)	1 370 107.6	IR(34) <sup>12</sup> C <sup>16</sup> O <sub>2</sub> -IP(26) <sup>12</sup> C <sup>16</sup> O <sub>2</sub>
3	2.5	2	4	3.5	3			
3	2.5	3	4	3.5	4	1 372 700.063(98)	1 372 699.2	IP(12) <sup>12</sup> C <sup>16</sup> O <sub>2</sub> -IP(10) <sup>13</sup> C <sup>16</sup> O <sub>2</sub>
3	3.5	3	4	4.5	4			
3	3.5	4	4	4.5	5	1 373 485.814(55)	1 373 485.2	IR(26) <sup>12</sup> C <sup>16</sup> O <sub>2</sub> -IR(28) <sup>13</sup> C <sup>16</sup> O <sub>2</sub>
5	4.5	4	6	5.5	5			
5	4.5	5	6	5.5	6	2 054 170.477(71)	2 054 170.0	IIP(38) <sup>12</sup> C <sup>18</sup> O <sub>2</sub> -IR(36) <sup>12</sup> C <sup>16</sup> O <sub>2</sub>
5	5.5	5	6	6.5	6			
5	5.5	6	6	6.5	7	2 054 944.054(82)	2 054 944.7	IIP(24) <sup>12</sup> C <sup>16</sup> O <sub>2</sub> -IR(18) <sup>12</sup> C <sup>16</sup> O <sub>2</sub>

<sup>a</sup>Partially resolved.

formation of relatively inert ions. The formation of metallic hydrides, among other factors, would appear likely to have a significant influence on the available concentration of the free metal. Hence, an astrophysical observation of MgH may be important to the understanding of significant chemical processes in molecular clouds.

Bernath, Black, and Brault<sup>4</sup> have recently performed a high resolution study of the  $A^2\Pi-X^2\Sigma$  transition of MgH using Fourier transform emission spectroscopy. Through careful measurement and analysis, ground state rotational transition frequencies were predicted with an estimated accuracy of  $\pm 30$  MHz, but asymmetric line profiles due to isotopic congestion and unresolved hyperfine structure, together with slight perturbations in the  $A^2\Pi$  state, limited the accuracy of their predictions. Although the degree of accuracy achieved is a considerable improvement over that of previous work, it does not quite reach the level necessary for unambiguous identification from interstellar spectra. The direct measurement of the rotational spectrum of MgH ( $X^2\Sigma$ ) would clearly be useful.

We have observed rotational spectra of the MgH molecule using our new tunable far infrared spectrometer. Tunable far infrared radiation is generated from the difference frequency between two CO<sub>2</sub> lasers using a tungsten-nickel point contact diode as the nonlinear mixing device. The far infrared radiation emitted from the diode is collected with a parabolic mirror, passed through a 19 mm i.d., quartz absorption cell 1 m in length, and detected with a helium cooled bolometer detector. Additional details about the spectrometer have been published elsewhere.<sup>5</sup> Magnesium hydride was produced in a dc discharge of 20 Pa (1 Pa = 7.5 mTorr) of H<sub>2</sub> over magnesium, run at 0.6 to 0.8 A. Even at these relatively high currents, it was necessary to thermally insulate the absorption cell in order to attain a sufficient vapor pressure of magnesium. Bright green emission due to atomic magnesium was readily observed while recording MgH spectra. To the best of our knowledge, these experi-

ments constitute the first observation of the pure rotational spectrum of an alkaline earth hydride.

Table I lists the observed transitions and their assignments, together with the CO<sub>2</sub> lasing lines used to synthesize the tunable FIR radiation. The data consist of two types of transitions: those for which  $\Delta F = \Delta J = 1$ , and those for which  $\Delta F = \Delta J = 0$ . The  $\Delta F = \Delta J = 1$  transitions, which are the strongest, usually appear as unresolved doublets due to the proton hyperfine structure. Only at low  $N$  do these doublets become resolvable outside the Doppler linewidth, and the highest transition for which these features can be discerned is the  $N = 3 \leftarrow 2$ . Their frequencies depend primarily on the rotational constants ( $B_0$  and  $D_0$ ) and spin rotation constants ( $\gamma_0$  and  $\gamma_D$ ), but are relatively insensitive to the hyperfine parameters. For the values of  $N$  observed here, the  $\Delta F = 0$  transitions are 20 to 40 times weaker than the  $\Delta F = 1$  transitions, but their frequencies are sensitive to the Fermi contact parameter  $b_F$  and their measurement therefore, provides the first gas phase determination of this quantity for MgH. The dipolar hyperfine interaction parameter  $t$  has been determined from ESR spectra in an inert gas matrix to be 0.9 MHz.<sup>6</sup> Thus, its contributions to the observed rotational transition frequencies are quite small, and this parameter is not determined here.

The Hamiltonian for a  $^2\Sigma$  molecule with nuclear spin  $I$  may be written

$$H = B_0 N^2 - D_0 N^4 + [\gamma_0 - \gamma_D N^2] \mathbf{N} \cdot \mathbf{S} + b_F \mathbf{I} \cdot \mathbf{S} + t [\mathbf{I} \cdot \mathbf{S} - 3I_z S_z] + c \mathbf{I} \cdot \mathbf{N},$$

where  $\mathbf{N}$  and  $\mathbf{S}$  are the rotational and spin angular momentum operators. The matrix elements of all terms except  $\gamma_D N^2 \mathbf{N} \cdot \mathbf{S}$  and  $c \mathbf{I} \cdot \mathbf{N}$  for  $S = I = 1/2$  are given by Carrington, Milverton, and Sarre<sup>7</sup> and those for the remaining two terms are given by Mizushima.<sup>8</sup> Table II gives the results of a least squares fit in which the value of  $t$  was constrained to the matrix value of 0.9 MHz. The value of  $c$  is not determined

TABLE II. Spectroscopic constants of  $^{24}\text{MgH}$  ( $X^2\Sigma^+$ )<sup>a</sup>.

	This work	Ref. 4
$B_0$	171 975.25(13)	171 974.8(16)
$D_0$	10.5857(10)	10.565(15)
$\gamma_0$	790.50(25)	791.5(39)
$\gamma_D$	0.159(10)	...
$b_F$	307.2(22)	296 <sup>b</sup>
$t$	0.9 <sup>b</sup>	0.9 <sup>b</sup>

<sup>a</sup>All values given in MHz.<sup>b</sup>Matrix ESR value; constrained in fit.

from the data which only provide the limits  $-100 \text{ kHz} < c < 200 \text{ kHz}$ . Using the parameters determined, all the observed transitions can be reproduced to within 1 MHz, as shown in Table I. The calculated values for the unresolved doublets are given as weighted averages of the individual computed frequencies using the theoretical intensities as weight factors. The residuals determined are somewhat greater than the quoted uncertainties in the unresolved line positions since the measured zero crossings may not be identical to this average. Nonetheless, the constants given reproduce the measurements to within a fraction of the observed linewidth and provide a satisfactory fit to the data. The rotational, centrifugal distortion, and spin rotation constants ( $B_0$ ,  $D_0$ , and  $\gamma_0$ ) are seen to be in good agreement with those obtained by Bernath *et al.*, but are an order of magni-

tude more accurate. The matrix value of the Fermi contact parameter is seen to be shifted 11 MHz from the true gas phase value determined here.

Measurement of lower rotational transitions of MgH are in progress. Although the signal-to-noise ratio decreases with decreasing  $N$ , a preliminary observation of the  $N=2 \leftarrow 1$  transition indicates that both the  $N=2 \leftarrow 1$  transitions, and perhaps a number of the components of the astrophysically important  $N=1 \leftarrow 0$  transition will be directly measurable. The additional data will provide further redundancy and a more reliable set of spectroscopic constants. Accurate measurements of other isotopic forms of MgH will provide a critical test of energy level theory for molecules in  $^2\Sigma$  states.

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## Spectroscopic and dynamical differences between exciplex and electronically excited EDA complex

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Electron donor-acceptor (EDA) systems are generally classified as EDA complexes if they exhibit stable ground state (with characteristic charge-transfer absorption), or as exciplexes if they do not. The formation of exciplexes is readily recognized by the appearance of a broad structureless fluorescence that accompanies electronic excitation of the donor or the acceptor molecule. Electronic excitation of the corresponding EDA complex, through its charge-transfer (CT) band, also leads to a featureless CT fluorescence.<sup>1</sup> Because of the spectral similarity of the fluorescence of  $b\pi-a\pi$  complexes (i.e., those between  $\pi$  donor and  $\pi$  acceptor) and the corresponding exciplex fluorescence, it is generally assumed that the fluorescent excited state of the EDA complex and the corresponding fluorescent exciplex are identical, in the absence of viscosity constraints that prevent the attainment of preferred donor-acceptor orientation.<sup>1,2</sup> The as-

sumption explicit to this conclusion is that there is no intrinsic (i.e., matrix-independent) potential barrier separating two possible minima. While this conclusion may be reasonable for some  $b\pi-a\pi$  EDA systems with limited ranges of cofacial donor-acceptor orientations (arrangement favored by CT interactions), its validity to EDA systems in general is questionable.

In this Communication, we present the results of our recent experiments on ether-tetracyanobenzene systems which demonstrate that the energetics and dynamics of the electronically excited EDA complex can be intrinsically different from those of the corresponding exciplex.

The experiments consisted of measuring time-resolved fluorescence spectra and energy-resolved fluorescence decay (by time-correlated photon counting), following excitation by a tunable picosecond laser.<sup>3</sup> 1,2,4,5-Tetracyanobenzene