D_2 E, F 1\Sigma_g^+(v' = 0 and 1) \rightarrow X 1\Sigma_g^+ (v'' = 0–5) Transition Energies for J' = J'' = 0–26: Comparison of Experiment and Theory

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The bimolecular gas-phase reaction between suprathermal atomic deuterium atoms and jet-cooled deuterium iodide, D + DI \rightarrow D_2 + I, was used to generate a wide range of rovibrationally excited deuterium molecules, D_2. Using (2 + 1) resonance-enhanced multiphoton ionization spectroscopy, we measured many previously unreported E, F 1\Sigma_g^+ (v'' = 0 and 1, J' = J'') \rightarrow X 1\Sigma_g^+ (v'' = 0–5, J'') two-photon transition energies, for rotational levels that range from J'' = 0 to 26. Experimental observation of many transitions corresponding to high rotational levels allowed the testing of higher-order molecular constants for the X 1\Sigma_g^+ ground state as well as for the E, F 1\Sigma_g^+ excited electronic state. Significant discrepancies were found between observed transition energies and those calculated from known molecular constants (i.e., more than a few hundred cm\(^{-1}\)) for the higher rotational levels. Separately, rovibrational term values of the X 1\Sigma_g^+ ground state and E, F 1\Sigma_g^+ state were calculated, using ab initio methods, to provide calculated transition energies. Excellent agreement is observed between the experimental and ab initio calculated transition energies, which confirms the accuracy of the theoretical potentials. © 1995 Academic Press, Inc.

INTRODUCTION

Characterization of the energy levels of molecular hydrogen and its isotopomers is a classic problem in molecular spectroscopy. The ground state of molecular hydrogen, the molecule of interest in this study, has been characterized in such detail that little would seem to remain unknown about its nature and energy levels. Although this assumption is true for low rotational levels over a wide range of vibrational states, whose energies are accurately known to within hundredths of cm\(^{-1}\) (1), it is not true for the higher rotational energy levels. Even for the X 1\Sigma_g^+ ground state, only the relatively low rotational levels J'' have been identified experimentally (typically J'' < 10 for v'' = 0–1) (1–4). As shown below, molecular constants derived from this limited set of data are not accurate enough to describe higher rotational energy levels.

The various electronic and rovibrionic levels of molecular deuterium have been identified using absorption and emission spectroscopy (3, 5–9), spontaneous Raman scattering (4), coherent anti-Stokes Raman scattering (CARS) (10), and resonance-enhanced multiphoton ionization (REMPI) spectroscopy (11–16). Various electronic states of D_2 have been characterized, and tables of rovibrionic term values have been compiled (17). So far, numerous electronic and corresponding vibrational states have been studied experimentally, but only a relatively small range of rotational states has been covered. Because of the large rotational constants of ground state molecular deuterium (B_0 \approx 30 \text{ cm}^{-1}), which result in widely spaced rotational energy levels,
only a few of the lowest rotational levels are populated at room temperature. Exciting molecular deuterium by using a discharge source leads to relatively little rotational excitation, although high vibrational levels can be populated in this manner (3). Thus, acquiring high rotational excitation of molecular deuterium requires the use of alternative methods.

A carefully chosen photodissociation or bimolecular reaction can efficiently generate highly rotationally excited molecules (10, 18, 19). For example, the H + HI → H_2 + I reaction has been used to generate highly excited rovibrational levels of H_2, whose ground state \( X^1Σ^+_g \) \((v^r, J^r)\) energy levels were subsequently identified using CARS (10) and \((2 + 1)\) REMPI spectroscopy via the \( E, F^1Σ^+_g \) electronic state (18). The latter \((2 + 1)\) REMPI detection scheme has been widely used for the determination of H_2 population distributions in combustion environments and for the study of gas-phase (18, 20–28) and surface reactions (29). For a somewhat limited set of rovibrational levels, this REMPI scheme has been used previously to detect D_2 as well (16, 20). This REMPI scheme enables ultrasensitive and state-selective detection of scattered reaction products and trace gases (27, 28, 30). However, reliable use of this scheme requires accurate knowledge and precise assignments of the transition energies for a broad range of rotational and vibrational levels.

Theoretical calculations are not hampered by the above-mentioned experimental obstacles, and high-level \( ab \) initio calculations have been reported for the \( X^1Σ^+_g \) ground state for a wider range of rotational levels than observed experimentally. Several high-level \( ab \) initio calculations show close agreement with experimentally established data for low rotational levels (31–35). In a recent study Yu and Dressler (35) calculated the rovibronic structures for all electronic states below the \( 1s + 2l \) dissociation limit, incorporating both adiabatic corrections and nonadiabatic coupling. Only rotational levels up to \( J = 5\) were considered, however.

The lowest \( ^1Σ^+_g \) excited electronic state of molecular deuterium, the \( ^1Σ^+_g \) \( E, F \) state, is characterized by a double-minimum potential. Both the inner well (\( E \) state) and the outer well (\( F \) state) support bound vibrational levels. In the inner well, four vibrational levels are located, \( v_E = 0, 1, 2, \) and 3, respectively, which correspond with \( v_{EF} = 0, 2, 6, \) and 9. The ordering of the vibrational levels in the inner and outer wells is \( J \)-dependent, however, as the rotational energy spacing in the outer \( F \) well is smaller than in the inner well. Recently, accurate characterization of the \( E, F^1Σ^+_g \) state has become an important parameter in the precise determination of the ionization potential of D_2 (4, 14, 36). Reported rovibrational levels of the \( E, F^1Σ^+_g \) state of molecular deuterium identified via emission spectroscopy generally cover a wide range of vibrational levels (3, 5), but once more the observed range of rotational levels is limited from, typically, \( J^r = 0 \) to 10. The currently used rotational constants (37) for the first two vibrational levels of the \( E \) state have been determined from this rather small range of rotational states. The \( E, F^1Σ^+_g \) state of molecular deuterium has also been characterized theoretically (35, 38–41).

In the present study we measured rovibrational population distributions of D_2 formed via the D + DI → D_2 + I reaction for \( v^r = 0 \) to \( v^r = 5\), observing rotational levels ranging from \( J^r = 0 \) to 26. D_2 was detected using \((2 + 1)\) REMPI spectroscopy via the \( E, F^1Σ^+_g \) state. The rovibrational distributions and velocity distributions of the D_2 products will be reported elsewhere (30). Here we compare experimentally determined \( E, F^1Σ^+_g \) \( (v^r = 0 \) and 1, \( J^r = J^r \)–\( X^1Σ^+_g \) \( (v^r = 0–5, J^r)\) transition energies, measured in units of cm\(^{-1}\), with our calculated values and with transition energies obtained from currently available molecular constants for the \( X^1Σ^+_g \) ground state and the \( E, F^1Σ^+_g \) excited state.
Experimental Procedures

REMPI spectra of D₂ were recorded using an ion-imaging apparatus described previously (42). In brief, DI (Cambridge Isotopes Laboratories, 99% D, backing pressure 8 psig [150 kPa]) is expanded supersonically into a source vacuum chamber through a solenoid valve (General Valve Series 9). Approximately 1 cm from the nozzle surface, the beam is skimmed (Beam Dynamics, orifice, 0.8 mm diameter) and collimated by a hole (1 mm diameter) in the repeller plate. The background pressure in the detection chamber is typically 10⁻⁶ Pa and increases to 10⁻⁵ Pa when the pulsed (30 Hz) DI molecular beam is on. Transitionally hot D atoms, formed in the beam via photolysis of DI, subsequently react with the residual DI in the beam to produce the D₂ (v, J) products; that is, the single beam expansion provides both reagents needed for the reaction. Under our experimental conditions, the collision energies for the D + DI reaction reach 3 eV. Additionally, the D + DI → D₂ + I reaction is exothermic by 1.46 eV. These conditions result in the formation of highly internally excited rovibrational product states of molecular deuterium.

In our experiments, a single ultraviolet laser pulse is used to photolyze the DI and to photoionize and detect the D₂ (v, J) products. Thus, photolysis, reaction, and state-selective product ionization occur during a single laser pulse (= 5-nsec duration). The laser wavelengths in the (2 + 1) REMPI spectra range from 204 to 236 nm. Generation of the required UV laser pulses is done by frequency doubling (Inrad) of an injection-seeded Nd:YAG-pumped dye laser (Spectra Physics GCR5, PDL 2) using KD*P crystals. The frequency-doubled dye output is sum-frequency mixed (Inrad) with the residual dye laser fundamental using appropriate BBO crystals. For the 204- to 233-nm wavelength range we use several dyes (R640, a mixture of R640 and DCM, DCM, and LDS 698). UV output powers are kept constant as much as possible at 300 ± 30 μJ per pulse. The bandwidth of the UV laser pulses is less than 1 cm⁻¹. Using dichroic mirrors, we cross the UV light with the molecular beam and focus it using a lens (f = 15 cm). After the state-selective photoionization of D₂ (v, J) molecules, D₂⁺ ions are accelerated along a 20-cm-long flight tube and impinge on a two-dimensional, position-sensitive detector. The detector consists of a pair of chevron microchannel plates (Galileo, 7.62 cm diameter) coupled to a fast phosphor screen (P47 Phosphor, 80-nsec decay time). Mass-selective detection of the D₂⁺ ions is accomplished by setting a boxcar gate on the D₂⁺ mass peak in the time-of-flight spectrum. The integrated phosphorescence of the phosphor screen, induced by impinging ions on the microchannel plates, is recorded using a photomultiplier tube.

Ab Initio Calculations

Theoretical transition energies are obtained from the differences between the ab initio rovibrational energies of the X ¹Σ⁺ and E, F ¹Σ⁺ states of D₂ plus the differences between their electronic term values (37). The rovibrational energy levels of each electronic state are obtained by solving the rovibrational Schrödinger equation for each pair of (v, J) energy levels. For the X ¹Σ⁺ state, the adiabatic potential tabulated by Schwartz and Le Roy (33), which includes both relativistic and radiative corrections, was used for the vibrational motion, and for the E, F ¹Σ⁺ state, the nonrelativistic adiabatic potential came from the work of Wolniewicz and Dressler (43). The Numerov–Cooley (see Refs. 44, 45) method was employed for the numerical solution of the one-dimensional Schrödinger equation of vibrational motion.
Note that analytical expressions for the nonadiabatic energy corrections of the rovibrational levels of the $X \ ^1\Sigma^+_u$ are available (33, 46). However, in view of the fact that the corresponding analytical corrections are not available for the $E, \ ^1\Sigma^+_g$ state (J5, 47), the present calculations employ the adiabatic approximation throughout, so that the transition energies are determined at a given level of approximation. Comparing our calculated adiabatic dissociation energies of the ground state with Wolniewicz's nonadiabatic results (46) available for $\nu = 0$–5 and $J \leq 10$, it is found that the nonadiabatic correction is dependent on $J$ and $\nu$. For $J = 0$, the nonadiabatic correction is 0.02 cm$^{-1}$ at $\nu = 0$ and increases to 0.27 cm$^{-1}$ at $\nu = 5$. For $J = 10$ the $\nu$-dependence is much weaker; the nonadiabatic correction varies from 0.68 cm$^{-1}$ at $\nu = 0$ to 0.81 cm$^{-1}$ at $\nu = 5$. Comparing the adiabatic energies of the $E$ state with the nonadiabatic results of Yu and Dressler (35) available for $J \leq 5$ shows that at $J = 0$ the difference is 1.34 and 1.88 cm$^{-1}$ for $\nu = 0$ and 1, respectively. At $J = 5$, the difference is 1.22 and 2.06 cm$^{-1}$. Thus the nonadiabatic corrections for the $E$ state are larger than those for the $X$ state. It is expected that the nonadiabatic corrections for the $E$ state levels will be larger at high $J$.

RESULTS AND DISCUSSION

More than 200 resonant transitions have been observed in the wavelength range studied. Part of the $D_2$ REMPI spectrum is shown in Fig. 1, together with some of the assignments. Only $Q$-branch transitions are observed. While $O$- and $S$-branch
### Table I
Calculated versus Observed $E, F, \Sigma_v^+$, $v_F = 0, J' = J'' - X, \Sigma_v^+$ ($v_F, J'$) Transition Energies (cm$^{-1}$)

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### Table II
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a. Experimentally obtained transition energies.

b. Calculated transition energies.

d. The two-photon transition energies (in cm$^{-1}$) of the observed $E, F, \Sigma_v^+$ ($v_F = 0, J' = J'' - X, \Sigma_v^+$) and $E, F, \Sigma_v^+$ ($v_F = 1, J' = J'' - X, \Sigma_v^+$) transitions are given, respectively. Because of the high center-of-mass collision energy and high exothermicity of the reaction used to generate the deuterium molecules, the D$_2$ products are formed with a broad range of translational energies (30). Therefore, the Doppler bandwidths of many of the observed transitions are close to 1 cm$^{-1}$, much broader than the laser bandwidth. Partly because of these

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broad bandwidths, some transition energies are observed to overlap. The wavelength of the UV laser was calibrated at a single frequency that corresponds to the \((2 + 1)\) Lyman \(\beta\) resonance of the D atom. The uncertainties in some of the experimental transition energies are therefore rather large, approximately 2 cm\(^{-1}\). The ion images reveal that some of the \(D_2\) is not formed in the bimolecular reaction, \(D + DI \rightarrow D_2 + I\), but via unimolecular photoinduced chemistry involving DI dimers or higher clusters. The role of cluster chemistry will be addressed in a future report (30), but has no consequences for the spectroscopy of the \(D_2\) molecule, as presented here. In Tables I and II, the experimentally observed transition energies are given.

In Figs. 2A and 2B the observed transition energies are compared with transition energies obtained using available molecular constants. We used the Dunham notation in which the term values may be expressed by (37)

\[
T_{\nu J} = T_{\nu J} + \Sigma_{\nu J} (v + \frac{1}{2})^J (J + 1)^{J}. \tag{1}
\]

The observed \(Q\)-branch transition energies \((J' = J')\) correspond to

\[
\Delta E = (T'_{\nu} - T_{\nu}) + \Sigma_{\nu J'} (v' + \frac{1}{2})^{J'} (J' + 1)^{J'} - \Sigma_{\nu J'} Y_{\nu J'} (v'' + \frac{1}{2})^{J''} (J'' + 1)^{J''}. \tag{2}
\]

Figures 2A (for \(v_0^J = 0\)) and 2B (for \(v_0^J = 1\)) show the differences, in cm\(^{-1}\), between the observed transition energies and those obtained using parameters from Bredohl and Herzberg for the \(X \, ^1\Sigma_g^+ (v^* = 0-5, J'^{J'})\) ground state (3) and parameters from Huber and Herzberg (37) for the \(E \, ^1\Sigma_g^+ (v_E^J = 0 \text{ and } 1, J'^{J'})\) excited state. Good agreement is observed between the experimental data and the data obtained from available spectroscopic constants for low rotational levels. Increasingly poor agreement is found, however, for higher rotational levels, which leads to deviations of more than several hundred cm\(^{-1}\) for \(J > 20\) (Figs. 2A and 2B). At these high rotational levels, the experimentally observed transition energies are significantly lower than those obtained using the above-mentioned molecular constants.

Also in Tables I and II, the transition energies are given obtained from our \textit{ab initio} calculations. In Figs. 3A (for \(v_0^J = 0\)) and 3B (for \(v_0^J = 1\)), the differences are shown between the observed and the \textit{ab initio} transition energies; very good agreement is found. In general the differences fall within a few cm\(^{-1}\). For higher \(J\) levels, slightly larger deviations seem to arise. These nonsystematic deviations may be caused partly by the weak intensities of these lines in the experimental spectra and the resulting difficulties in assigning them accurately. On the other hand, our calculations did not take nonadiabatic coupling or relativistic effects into account for the \(E, F \, ^1\Sigma_g^+\) state. Relativistic effects are expected to be very small. Nonadiabatic coupling, however, can be large, especially for the high \(J'^{J'}\) levels of the \(E, F \, ^1\Sigma_g^+\) state, because of interactions with other nearby excited states (35). Therefore, some of the discrepancies between the observed and calculated transition energies may be genuine, because the measurements reveal the true \(E, F \, ^1\Sigma_g^+ - X \, ^1\Sigma_g^+\) transitions, whereas the calculations are based on adiabatic energy levels.

The data presented in Fig. 2 clearly show the inadequacy of published molecular constants in describing the observed transition energies for high \(J\). As mentioned above, rotational molecular constants for the \(X \, ^1\Sigma_g^+\) and the \(E, F \, ^1\Sigma_g^+\) state have been determined from low rotational levels. These constants are probably accurate for \(B\), and to some extent for \(D\), but they are not very accurate for \(H\), which becomes an increasingly important parameter for the higher rotational levels. The data presented in Figs. 2A and
2B reveal indirect information on the accuracy of the molecular constants used for the $X^1\Sigma^+_g$ ground state. The depicted transition energy differences corresponding to the various ground state vibrational levels, $v''$, should overlay exactly if the ground state parameters used were “perfectly” correct. The data shown in Fig. 2A reveal that the $v'' = 1$ data in particular deviate significantly from the other $v''$ data. This divergence is confirmed by the data presented in Fig. 2B. Interestingly, $D_{v''=1}$ derived from experimental results by Bredohl and Herzberg (J) was shown to be too low to fit on a continuous plot of $D_{v'}$ versus $v''$. Our experimental data support a relative upward correction for $D_{v''=1}$, which would bring the data in Figs. 2A and 2B in better agreement with each other.

Description of the energy levels of the $E$ well of the $E, F^1\Sigma^+_g$ state by means of
molecular constants is valid only for low values because the higher f levels are

(1) exact scale
(2) exact scale in the transition energies to the observed (cm$^{-1}$).

(1) transition energies to the observed (cm$^{-1}$).

(2) transition energies to the observed (cm$^{-1}$).
1, including in the fit only rovibrational energies of $J'$ levels "reasonably" far below the barrier. For $v' = 0$, the lowest 27 levels were used ($J' = 0$–26) and for $v' = 1$ the lowest 19 rotational levels were used. Figure 4 depicts the energy differences between the rovibrational energies calculated by directly solving the rovibrational Schrödinger equation and those energies obtained using the molecular constants derived from the lower range of $J'$ levels. Clearly, the derived molecular constants describe the rotational energy levels of the $E$ well quite accurately up to $J' = 23$ for $v' = 0$ and up to $J' = 15$ for $v' = 1$. As shown, the deviations become dramatic and nonsystematic for higher $J'$ levels, which indicates that the single-well description used in the fit is no longer appropriate for these $J'$ levels. Our limited experimental data on the higher $J'$ levels confirm the calculated effects. Unfortunately, no transition energies were observed for $J'$ levels above 26 for $v' = 0$ and above 21 for $v' = 1$; such observations would have allowed us to test these theoretical findings in more detail.

In addition, the observed ion intensities (not shown) (30) allow us to compare the relative two-photon transition moments for the $E, F^1 \Sigma_u^+ (v_F = 0, J' = J')$–$X^1 \Sigma_g^+ (v', J')$ and $E, F^1 \Sigma_u^+ (v_F = 1, J' = J')$–$X^1 \Sigma_g^+ (v', J')$ transitions. Because of the multiphoton nature of the detection scheme, intensities obtained from the observed ion signal are not straightforward. To obtain signal intensities, the laser power was kept constant as much as possible. Spectra were then normalized for laser power dependence using previously obtained correction factors; that is, the ion signals were found to be proportional to the laser pulse energy raised to a power of 1.4 (16). Table III lists the experimentally observed and calculated relative intensity ratios. Again, the agreement between the experimental and theoretical data is very good. In general, the transitions via the $E, F^1 \Sigma_u^+ (v_F = 0)$ intermediate level are much stronger than those via the $E, F^1 \Sigma_u^+ (v_F = 1)$ intermediate level for $v' = 1, 2, \text{ and } 3$ vibrational levels of the $X^1 \Sigma_g^+$ ground state. For $v' = 4 \text{ and } 5$, however, the scheme using the $E, F^1 \Sigma_u^+ (v_F = 1)$ intermediate level is the more sensitive choice for detection by $(2 + 1)$ REMPI spectroscopy.

![Fig. 4. Energy differences (cm$^{-1}$) between rovibrational energies of the $E, F^1 \Sigma_u^+ (v_F = 0 \text{ and } 1)$ state obtained by directly solving the rovibrational Schrödinger equation and those energies calculated using molecular constants obtained from a limited set of rovibrational energies (corresponding to lower $J'$ values). See text for further explanation.](image-url)
TABLE III

<table>
<thead>
<tr>
<th>v'</th>
<th>Intensity ratio calculated E, v' = 0 : E, v' = 1</th>
<th>Intensity ratio experimental E, v' = 0 : E, v' = 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.3 : 1</td>
<td>1.52 : 1</td>
</tr>
<tr>
<td>2</td>
<td>6.2 : 1</td>
<td>9.2 : 1</td>
</tr>
<tr>
<td>3</td>
<td>8.1 : 1</td>
<td>11 : 1</td>
</tr>
<tr>
<td>4</td>
<td>0.7 : 1</td>
<td>1 : 1</td>
</tr>
<tr>
<td>5</td>
<td>1 : 4.8</td>
<td>1 : 4.2</td>
</tr>
</tbody>
</table>

*Calculations were carried out for J = 8 only; experimental values are averaged over a range of rotational levels J, typically J = 5 to 10. Errors in the experimental ratios are up to 25%.

CONCLUSIONS

Using a gas-phase bimolecular reaction, D + DI → D₂ + I, a wide range of rovibrational levels of D₂ can be populated. This approach has allowed us, using (2 + 1) resonance-enhanced multiphoton ionization spectroscopy, to observe new E, F ¹Σ⁺⁺ (v' = 0 and 1) - X ¹Σ⁺⁺ (v" = 0 - 5, J") two-photon transition energies for rotational levels that range from J" = 0 to 26. Our experimental data are used to examine reported values for molecular constants for the X ¹Σ⁺⁺ ground state as well as the E, F ¹Σ⁺⁺ state. Poor agreement is found for high rotational levels. Rovibronic term values of the X ¹Σ⁺⁺ ground state and E, F ¹Σ⁺⁺ state were calculated, using ab initio methods, providing calculated two-photon transition energies. Excellent agreement is found between the observed and ab initio transition energies. Therefore, the adiabatic potentials tabulated by Schwartz and Le Roy (33) for the X ¹Σ⁺⁺ state and by Wolniewicz and Dressler (43) for the E, F ¹Σ⁺⁺ state describe the rotational energy levels, at least for relatively low vibrational levels, extremely well, even for very high J values. Experimental and theoretical results reveal the influence of the F outer well on the energy levels of the inner E well. Reasonably far below the barrier between the E and F wells, perturbations by the F well levels do not lead to significant energy shifts of the E well levels. At rotational levels close to or above the barrier, the effects induced by the presence of the outer F well are quite dramatic, and the rovibrational energy levels can no longer be described by a single potential well.

Measured and calculated signal intensities reveal that when applying the (2 + 1) E, F ¹Σ⁺⁺ - X ¹Σ⁺⁺ REMPI scheme for D₂ detection the v' = 0 intermediate level is the appropriate choice for detection of X ¹Σ⁺⁺ (v" = 1 - 3) rovibrational levels, whereas the v' = 1 intermediate level is the better choice for detection of X ¹Σ⁺⁺ (v" = 4, 5) rovibrational levels.

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46. L. Wolniewicz, submitted for publication.