The relative importance of temperature and isotope effects on the dipole oscillator strength distribution of H_2

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Summary. The calculation of the effects of temperature and isotopic composition on the energy weighted moments of the dipole oscillator strength distribution of H_2 in the random phase approximation to the polarization propagator are reported. It is seen that the effect of isotopic composition is small, while that of temperature is of an order accessible to experiment. We find that all the mean excitation energies I_μ, for $\mu = -1, 0, 1$, decrease with temperature as does the dipole oscillator strength moment $S(\mu)$ for $\mu > 0$, while the opposite is true for $\mu < 0$. These effects are interpreted in terms of the bond length dependence of the excitation energies.

1. Introduction

As advances in computing hardware and software design have made studies of electronic structure a tool rather than an end in itself, interest in the community of theorists has shifted from calculation of geometric and electronic structure to studies of properties and dynamics. Jan Linderberg, to whom this contribution is dedicated, has been influential in both of those fields. In the following, we discuss the problem of temperature and isotope effects on some moments of the dipole oscillator strength distribution (DOSD) of the hydrogen molecule, and use the polarization propagator for the calculation of the requisite excitation properties. We will be concerned specifically with the origin of these two effects in nuclear motion, and with the relative importance of the two effects and their absolute magnitudes with regard to whether or not they may be experimentally observable.

Although many body techniques have been used for many years in solid state physics and statistical mechanics [1], it was Jan Linderberg [2–4] in collaboration with Öhrn [5–7] and with his students [8] that brought the polarization propagator formalism to bear on molecular problems. As this method has proved so fruitful over the years [9, 10], especially for calculation of excitation properties of molecules, it is this method that we choose to employ here.

The energy weighted moments of order μ of the dipole oscillator strength distribution of a molecule are defined as

$$S(\mu) = \int E^{\mu} \frac{\mathrm{d}f}{\mathrm{d}E}\,\mathrm{d}E, \tag{1}$$

$$L(\mu) = \int E^{\mu} \ln E \frac{\mathrm{d}f}{\mathrm{d}E}\,\mathrm{d}E \tag{2}$$

and

$$\ln I_{\mu} = \frac{L(\mu)}{S(\mu)}, \tag{3}$$

where E and f label the excitation energies and dipole oscillator strengths of the system, respectively. Quantities such as these moments are interesting as they are related to many of the quantities characteristic of the interaction of radiation with matter, such as swift ion stopping and straggling, the Lamb shift, electronic excitation, and static polarizability [11, 12]. Although there is considerable interest in these quantities, they are difficult to calculate due to the necessity of having the *complete* DOSD available. Thus, most of the DOSD's available for molecules have been obtained by semi-empirical means, typified by the work reported in the series of papers by Meath and co-workers [13]. On the other hand, the polarization propagator provides a scheme whereby a set of transitions and pseudo-transitions representing the entire excitation spectrum of a molecule can be calculated, using a discrete representation of the continuum. Although individual the pseudo-transitions into the continuum as calculated here have no physical significance (as opposed to the actual spectrum of transitions), their integrated moments do, and the scheme can be used to calculate the energy weighted moments mentioned above.

Previously we have been concerned with calculation of energy weighted moments of the DOSD and of molecular properties related to them, in particular the mean excitation energy for stopping, I_0. We have found [14–16] that many of the moments have significant variation with internal nuclear coordinate. Assumption of a Boltzmann population of rovibrational levels leads to the conclusion that the moments should exhibit a temperature dependence. In fact, such a dependence has been predicted for the stopping of low energy protons in hydrogen [16]. The origin of the temperature dependence is related to the changing average bond length in the molecule with temperature. This is a consequence of varying population of various rovibrational levels, which correspond to different mean internuclear distances arising from the asymmetric molecular potential. One might, then, expect that various isotopomers, having somewhat different effective molecular potentials, would also have somewhat different energy weighted moments of the DOSD. Although such differences are not expected to be large, recent advanced in experimental techniques will soon make them accessible. In fact, there has been some indication [16] that for the case of energy deposition, related to the I_0 moment (*vide infra*), a temperature effect might be observed. There are also experimental reports of a possible small difference in stopping of protons in H_2 and D_2 for low energy (< 20 keV) protons [17], and in the charge exchange and ionization cross sections of H_2 and D_2 for low energy (< 30 keV) protons and deuterons [18].

We concern ourselves here with an investigation of temperature dependence of $S(\mu)$ and I_{μ} for the isotopomers H_2, HD and D_2, with particular emphasis on the

relative importance of the isotope and temperature effects. We use the polarization propagator formalism pioneered by Jan Linderberg as the primary tool.

2. Methodology

As we employ the Born–Oppenheimer approximation, the electronic structure, and consequently the DOSD and electronic potential, of the molecule under consideration is independent of the isotopic composition. The only place that the nuclear masses enter the theory is in the solution of the Schrödinger equation for the rovibrational states used in the temperature averaging. The differences in spectral moments among isotopomers reported below are thus purely consequences of finite temperature.

2.1. The DOSD

In order to calculate the spectral moments of the DOSD defined in Eqs. (1)–(3), the complete set of molecular electronic excitations from the ground state $|0\rangle$ to excited state $|n\rangle$ with excitation energies $\{E_{0n}\}$ and associated oscillator strengths $\{f_{0n}\}$ is needed. We obtain these, in the dipole length formulation, from the polarization propagator, defined as [9, 10].

$$\langle\langle r_a; r_b\rangle\rangle_E = \sum_{n \neq 0} \left[\frac{\langle 0|r_a|n\rangle\langle n|r_b|0\rangle}{E - E_n + E_0} - \frac{\langle 0|r_b|n\rangle\langle n|r_a|0\rangle}{E + E_n - E_0} \right], \tag{4}$$

where r_a is a component of the dipole operator. From the poles and residues of the propagator, we can determine the excitation energies $(E_0 = E_n - E_0)$ and transition moments ($\langle 0|r|n\rangle$), from which the dipole length oscillator strengths can be calculated

$$f_{0n}^L = \frac{2E_0}{3} \langle 0|r|n\rangle \cdot \langle n|r|0\rangle. \tag{5}$$

All quantities are in Hartree atomic units.

We solve the equation of motion for the propagator perturbatively, using the fluctuation potential as the perturbation [10]. Experience shows [19–22] that correlation is needed in order to calculate reliable spectral moments of the DOSD. One needs to calculate the propagator at least in the consistent first order approximation to the propagator which is identical to the random phase approximation (RPA). At this level correlation is added in both ground and excited states in a balanced way, and we achieve accuracy high enough for our purposes (*vide infra*).

The polarization propagator is evaluated using a finite basis set. The basis used in these calculations is the contracted $(9s6p3d)$ Gaussian basis of Jaszunski and Roos [23] which we have used previously [15] for calculations on H_2. The set admits 89 particle–hole excitations which yields a finite number of excitations equal to the number of allowed particle–hole excitations. As a result of the finite basis, we approximate the continuum with a finite number of discrete excitations placed such that they represent the continuum. We have found this scheme to give good results [19] for properties of the dipole oscillator strength distribution where we evaluate quantities which depend on sums over all excited states. However, no

physical significance can be attached to individual continuum pseudostates obtained in this way.

Calculations were carried out on H_2 at 21 internuclear distances ranging from 0.3 to 5.0 a.u. using the MUNICH [24] system of programs. Mean excitation energies, and the S and L moments, defined in terms of the dipole oscillator strengths (f_{0n}) and excitation energies (E_0), were calculated directly as a discrete sum over states, e.g.

$$\ln I_0 = \frac{\sum f_{0n} E_{0n}}{\sum f_{0n}}. \tag{6}$$

2.2. Temperature averages

To find the average of a property over the Boltzmann distribution of populations in the accessible rovibrational states at a particular temperature, one first calculates the expectation values of the property, P over the radial rovibrational function $\xi_{v,J}(R)$

$$P(v, J) = \langle \xi_{v,J}(R) | P(R) | \xi_{v,J}(R) \rangle, \tag{7}$$

where $\xi_{v,J}(R)$ is obtained from the one-dimensional Schrödinger equation

$$-\frac{\hbar^2}{2m} \frac{d^2 \xi(R)}{dR^2} + \left(U(R) + \frac{\hbar^2}{2m} \frac{J(J+1)}{R^2} - E(v, J) \right) \xi(R) = 0 \tag{8}$$

using the method of Numerov and Cooley [25, 26]. Here $U(R)$ is a cubic taught-spline fit to the electronic ground state potential function of Kolos and Wolniewicz [27–29], m is the reduced mass of the pertinent isotopomer, v is the vibrational quantum number and J is the end-over-end rotational quantum number. Thermal averages at temperature T are then computed as Boltzmann averages over states of energy $E(v, J)$ (calculated from Eq. (8)) with degeneracy $g(J)$,

$$\langle P \rangle = \frac{\sum_{v,J} g(J) e^{-E(v,J)/k_B T} P(v, J)}{\sum_{v,J} g(J) e^{-E(v,J)/k_B T}}. \tag{9}$$

3. Results and discussion

The results of this investigation are presented in Figs. 1–4. Although we have calculated the $S(\mu)$ and I_μ moments for $-6 \leqslant \mu \leqslant 2$, it is our experience [20, 30] that the higher moments begin to be in error due to the powers to which the pseudo-state excitation energies are raised. Furthermore, $S(0)$ has no temperature dependence: it is the Thomas–Reiche–Kuhn sum rule. The moments $S(1)$ and $S(-1)$ vary less with isotopic composition than does $S(-2)$ [15], which corresponds to the static polarizability of the system. I_1 and I_0 are the mean excitation energies for straggling and stopping. As representative of the moments we consequently report isotopic and temperature dependence of $S(-2)$, I_1, I_0 and I_{-1}.

As the rovibrational averages presented here depend essentially on bond length a comment on the accuracy of the RPA over the appropriate range of bond lengths is appropriate. It is well known that the RPA gives the best results near the potential minimum, and begins to deviate at longer bond lengths as the excitation energies $E_{0n}(R)$ tend to be too small at large distances. This leads, for example, to
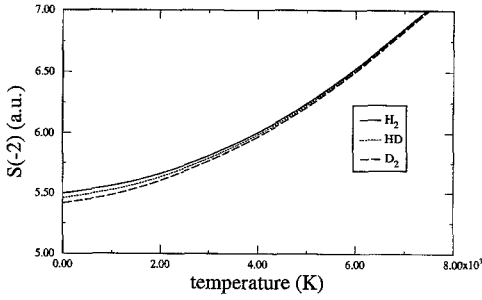
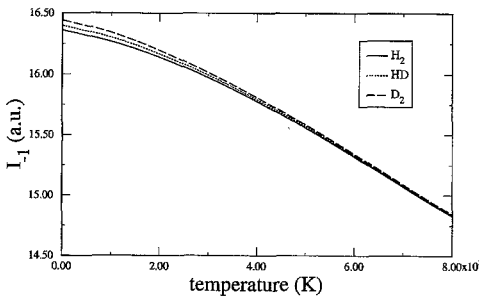**Fig. 1.** S_{-2} as a function of temperature for H_2, HD and D_2

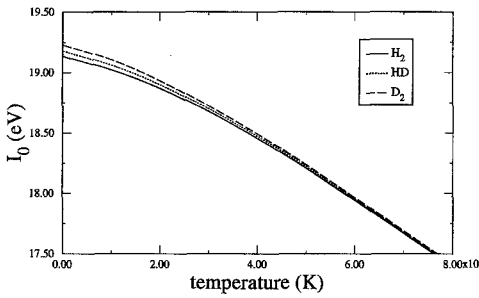**Fig. 2.** I_1 as a function of temperature for H_2, HD and D_2

Fig. 3. I_0 as a function of temperature for H_2, HD and D_2
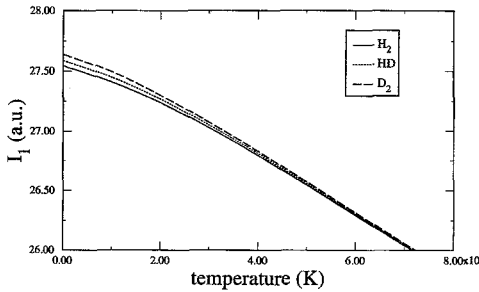

Fig. 4. I_{-1} as a function of temperature for H_2, HD and D_2

Table 1. Maximum percent variation due to temperature and isotopic composition of some moments of the DOSD

Moment	Temperature variation[a] (% of the $T = 0$, H_2 values)	Isotopic variation[b] (%)
$S(1)$	8.1	0.4
$S(-1)$	12.7	0.6
$S(-2)$	30.0	1.5
I_1	6.3	0.3
I_0	9.1	0.5
I_{-1}	9.4	0.5

[a] Maximum variation over the temperature range 0–8000 K for the isotopomer with the largest variation
[b] Maximum variation between H_2 and D_2 isotopomers at any temperature

values of $S(-2)$ which are too large [31] (by up to a factor of 3) with respect to more sophisticated methods at large R. However, we do not expect that errors in the moments at large bondlength will affect the results reported below. The vibrational levels with a Boltzmann factor > 0.01 ($v \leqslant 4$) all have outer classical turning points at small enough distances that our result differs by 10% or less from accurate values [31], indicating that calculation of the moments to higher accuracy at large distances would not be expected to alter the result presented here.

The magnitudes of the isotope and temperature effects on $S(-2)$, $S(-1)$, $S(1)$, I_1, I_0 and I_{-1} are given in Table 1. The isotope effect is calculated as the difference between the values of the property between H_2 and D_2, while the temperature variation is calculated as the variation (as a percentage of the $T = 0$, H_2 values) over the temperature range 0–8000 K for the isotopomer with the largest variation. Although the temperature averaging can easily be done to higher temperatures, kT becomes approximately 20% of the binding energy at 10 kK, so, in order to avoid problems with dissociation (which is on the order of a percent at this temperature) we present results only to 8000 K. In addition, the question of experimental verification above these temperatures becomes moot. The clear conclusion, from either the table or the figures, is that the isotope effect, while extant, is at least an order of magnitude smaller than is the variation due to temperature. The temperature variation is approximately a 10% effect at 8000 K, and thus in principle measurable, while the isotope effect seems to be below present detection limits.

The temperature dependencies of the moments of the DOSD presented in Figs. 1–4 can be traced ultimately back to the dependence of the excitation energies of the system on the geometry, in this case bond length, of the molecule. First it is convenient to relate them to the average molecular bond length as a function of temperature. Due to the skewness of the ground state potential, the average bond length increases with increasing rovibratioinal quantum numbers. That is, $\langle R \rangle$ increases with T as displayed in Fig. 5. As $S(-1)$ is proportional to $\langle R \rangle$, it increases with temperature as well. The same holds for other negative μ moments of $S(\mu)$. As $S(\mu)$ has energy weighting $E^{\mu+1}$ (Eqs. (1) and (5)), for moments with $\mu < 1$ the low energy contributions are weighted most, and the negative moments increase with increasing bondlength. This is consistent with a decrease in E_{0n} as $\langle R \rangle$ (or T) increases, which is a well-known phenomenon in diatomic molecules. We believe that it is this effect that determines the temperature dependence in the $S(\mu)$ moments rather than the direct bond length effects in the transition moments.
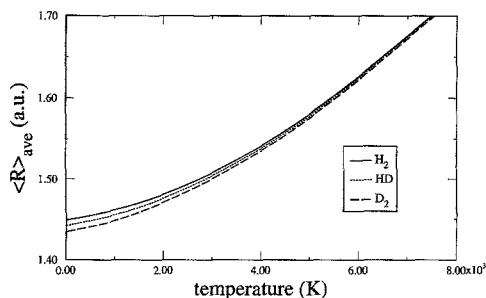
Fig. 5. Average bond length as a function of temperature for H_2, HD and D_2

An example is shown in Fig. 1. The opposite behavior occurs for the positive moments.

In Figs. 2–4 it can be seen that all the mean excitation energies (I_μ, $\mu = -1, 0, 1$) decrease with temperature. That is, they have the same behavior as the positive $S(\mu)$ moments. Thus the corresponding three $L(\mu)$ moments all must have the same functional behavior. Further, $L(1)$ must decrease with $\langle R \rangle$ (or T) faster than does $S(1)$ (see Eq. (3), although, as the ratio occurs in the exponent, the relative change can be small.

The behavior of $L(\mu)$ for $\mu = -1, 0$ can be understood from the decrease in E_{0n} with increasing T (or $\langle R \rangle$) and the $E_{0n}^{\mu+1} \ln E_{0n}$ energy dependence of $L(\mu)$. As can be seen from Eqs. (2) and (5) the $E_{0n}^{\mu+1} \ln E_{0n}$ weights the high energy region of the spectrum of pseudostates most, leading to decreasing (more negative) values of $L(\mu)$ for $\mu \geqslant -1$. The relative changes in magnitudes of $L(1)$ and $S(1)$ as a function of R is in qualitative agreement with what we found for the same ratio for other molecules [15]. That is, $L(\mu)$ is more energy-dependent than is $S(\mu)$ for $\mu > 0$. We also observe that the temperature dependence of I_0 is consistent with the observation that the mean excitation energy must decrease from the molecular value at ambient temperature (19.10 eV at 300 K as calculated here) to the atomic value of 14.99 eV [32] in the dissociation limit.

As the average bond length of H_2 at given temperature varies inversely with isotopic mass, the bond length for H_2 is always the longest at fixed temperature, and consequently has the largest value for $S(-2)$ of the isotopomers, and the smallest values of I_1, I_0 and I_{-1}, according to the above arguments.

Finally, as far as we are aware, temperature or isotope effects on the moments of the dipole oscillator strength distribution of molecules have never been measured. This is undoubtedly due to the small variation of these moments over small temperature range. For example, cryogenic and ambient temperature measurements differ by less than 500 K, which gives rise of changes of only 0.3% in e.g. I_0, a difference well within error bars in a stopping measurement.

4. Summary

We have presented polarization propagator calculations of the temperature and isotopic dependence of some energy weighted moments of the dipole oscillator strength distribution of H_2. Due to the anharmonicity of the internuclear potential and the large ratios of mass differences among the possible isotopes, H_2 should be a very favorable case for finding temperature and isotope dependent variations in

the moments. We see that the isotope effect is small, typically $< 1\%$, while the temperature effect is of the order of 10%, in the experimentally accesible range.

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