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Electron Compton-like quasielastic scattering from H_2, D_2, and HD

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A significant anomaly in the ratio of the cross sections for quasielastic scattering of D_2 to H_2 in a 50:50 mixture has been reported recently [Phys. Rev. Lett. **100**, 043204 (2008)]. In particular, the interpretation of quasielastic scattering provided in that work predicts that the signals should be based on the elemental content and not on the molecular structure, and thus the spectrum for HD and that for the 50:50 mixture should be effectively the same, aside from minor line shape differences. In fact the signal from H in the mixture was low by 31(4)% (or that from D was correspondingly high) when compared to the signal from H in HD. Here, an attempt is made to explain this anomaly by scattering theory calculations based on the first Born and Born–Oppenheimer approximations. The relative contributions of translational, vibrational, and rotational excitations are computed for several temperatures. The computed signals are compared to the experimental spectra of HD and the 50:50 H_2/D_2 mixture and to pure H_2 and D_2, which were reported previously. Good agreement is found for the spectral line shapes. The predicted peak positions are also found to be in good agreement with experiment except for a slight shift in the case of D_2. However the anomalous cross section ratio of D_2 to H_2 experimentally observed in the 50:50 mixture could not be explained by this approach. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3108490]

I. INTRODUCTION

Electron energy loss spectra at near zero energy loss recorded from both gaseous[1–4] and solid[5–9] multielement samples at large momentum transfer (high impact energy and large scattering angle) exhibit multiple peaks with energy separations that increase with increasing momentum transfer. These types of signals are called quasielastic electron scattering. The number and energy separation of these signals are explained qualitatively by Rutherford scattering theory,[10] which is based on conservation of energy and momentum in *binary* collisions of the incident particle within the assumption that the electron scatters independently from each atom of the target system. Although this is an approximation, the nuclear-nuclear interference scattering, which is also present, is small at large *K*. Note that the approach taken here does not assume that each nucleus scatters independently.

A recent study of quasielastic electron scattering by H_2, D_2, and HD (Ref. 4) found that the ratio of the cross section for D_2 to that for H_2 in a 50:50 mixture was 31(4)% larger than the ratio of the H to D signals observed in the quasielastic scattering spectrum of HD. Conditions for the experiments were chosen to limit the scattering to Rutherford scattering from the nuclei. By using sum rule normalization of the signals from H_2, D_2, and the 50:50 mixture, we show that the H_2/D_2 intensity ratio in the mixture is anomalous, without reference to the HD data. Although it was speculated in Ref. 4 that the anomaly was related to nuclear spin effect specific to H_2, a numerical or analytic theoretical calculation of this effect was not made in that work. Here we present details and results of a calculation of the quasielastic scattering spectrum of H_2, D_2, and HD within the framework of conventional quantum chemistry. The computational and experimental results are compared in order to see if conventional quantum mechanics and scattering theory can explain these observations.

Anticipating the outcome, we note that, although the methods we have used predict accurately the shape and positions of the quasielastic peaks of H_2, D_2, and HD, there is still a significant deviation between the predicted and observed intensities. Since nuclear spin effects are included in the present approach, the speculation of nuclear spin effects as the origin of the intensity anomaly made earlier[4] is not supported by the model adopted in this work. This suggests that, whatever the origin of the anomalous intensity, it may be a general phenomenon. Anticipating our final conclusion, one effect that might explain the anomaly within the present picture is if the H_2/D_2 sample did not contain an equilibrated mixture of ortho and para isomers. In particular the observations could be explained if the H_2 in the sample was equilibrated at a temperature well below 85 K and allowed to warm up to 298 K in the absence of a suitable catalyst. However this seems very unlikely since two separate gas samples with different histories gave the same result.

II. THEORETICAL MODEL

The goal is to predict the shape, position, and amplitude of the quasielastic peaks in electron scattering by a neutral molecule where the incident electron energy and momentum transfer are chosen to be so large that only Coulomb scatter-

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ing from the bare nuclei is important. This type of scattering is referred to as quasielastic scattering. It is similar to Compton scattering[11–14] in that energy and momentum are conserved, giving rise to a delta function-like contribution from each nucleus which is then broadened by the translational (T), rotational (R), and vibrational (V) motions induced in the scattering. The quasielastic peak has the following characteristics.

1. Scattering from atoms, where only translational excitation can occur, is very different than that from molecules, where, in addition, rotational and vibrational excitation occurs.
2. Nuclei with different masses give rise to broadened peaks centered about different energy losses, where the shift is given by the Rutherford expression. This is apparently quite different from elastic scattering by molecules at low momentum transfer where all contributions are centered about the same energy loss and only differ in their peak widths, which reflect differences in their velocity distributions.
3. The broadening from rotational and vibration excitation is discrete below the bond dissociation energy. However, broadening due to translational excitation may make it difficult to observe discrete rovibrational structure since each line is broadened and shifted to higher energy loss by translational excitation.

While quasielastic scattering from solids was observed a long time ago,[5] it has only recently been observed in the gas phase.[1–4] An earlier paper[15] predicted the existence of a shift of the elastic line due to excitation of vibrational states associated with the ground electronic state for diatomic molecules but did not properly consider the role of translational and rotational excitation on quasielastic scattering.

In the following, we first consider the sum rules of the generalized oscillator strength (GOS) for electron scattering[16] and how they apply to quasielastic scattering.[17–21] This is done because these sum rules, which are energy loss moments of the scattering signal, can in some cases be calculated from ground state wave functions without any assumptions as to the nature of the excited states involved other than the validity of the first Born approximation of scattering theory. This section is followed by the first Born approximation treatment of quasielastic scattering in which the Born–Oppenheimer approximation is employed to break down the total quasielastic scattering signal into separate translational, rotational, and rovibrational components. In the cases of H_2 and D_2, nuclear spin symmetry requirements and their effects on the scattering intensities are incorporated. We then compare the predicted integrated intensities to the sum rules to show that the results are internally consistent. Finally we compare the predicted spectra to experiment.

A. Sum rules for GOSs

A number of sum rules[16–21] exist within the framework of the first Born approximation of scattering theory. These sum rules are based on the GOS $[f_{\mathrm{el}}(E,K)]$, defined in terms of differential cross sections for electron scattering, $d^2\sigma_{\mathrm{el}}/dEd\Omega(E,K)$, as

$$f_{\mathrm{el}}(E,K)=K^2E\frac{k_0}{k_1}\frac{d^2\sigma_{\mathrm{el}}(E,K)}{dEd\Omega}, \tag{1}$$

where E is the energy loss, k_0 is the incident electron momentum, k_1 is the final electron momentum, K is the momentum transfer, and the subscript "el" denotes quasielastic scattering. For quasielastic scattering $k_0/k_1=1$, the dependence of the momentum transfer (K) on the energy loss, E, can be neglected; hartree atomic units (1 a.u. energy = 27.21 eV) are used throughout this paper. The differential cross section can be defined within the independent atom model (IAM) (Ref. 22) as

$$\frac{d^2\sigma_{\mathrm{el}}}{dEd\Omega}(E,K)=\sum_{n=0}^{\infty}\sum_{n'=0}^{\infty}\left|\langle\Psi_{\mathrm{on}}^{TRV}|\sum_{q=1}^{N}Z_q^{\mathrm{eff}}e^{i\vec{K}\cdot(\overrightarrow{R_{\mathrm{cm}}}+\overrightarrow{R_q})}\times|\Psi_{\mathrm{on}'}^{TRV}\rangle\right|^2\delta(E+E_{\mathrm{on}}-E_{\mathrm{on}'})/K^4, \tag{2}$$

where $Z_q^{\mathrm{eff}}=Z_q-F_q(K)$ is the effective charge on the qth nucleus, Z_q is the nuclear charge, and $F_q(K)$ is the x-ray coherent scattering factor for the qth atom.[22] The IAM approximation neglects the effects of chemical binding on the electron density. This should be an excellent approximation in the high-energy, large momentum transfer (high scattering angle) limit. Here Ψ_{on}^{TRV} describes the translational, rotational, and vibrational motions of the initial state, and $\Psi_{\mathrm{on}'}^{TRV}$ describes these motions in the excited state where $\overrightarrow{R_{\mathrm{cm}}}$ is a vector from the origin of the laboratory frame to the center of mass of the molecule, and $\overrightarrow{R_q}$ is a vector from the center of mass to the qth nucleus. The sum over the energy loss E_{on} is an average over all thermally populated initial states, while the sum over the energy loss $E_{\mathrm{on}'}$ is over all translational, rotational, and vibrational excited and de-excited (super elastic collisions) final states which are created from the states initially thermally populated. The quasielastic GOS should obey the sum rules,

$$S_{\mathrm{el}}(0,K)=\int_0^{\infty}dEf_{\mathrm{el}}(E,K)=\sum_{q=1}^{N}\frac{Z_q}{2M_q} \tag{3}$$

and

$$K^2S_{\mathrm{el}}(-1,K)=K^2\int_0^{\infty}dEf_{\mathrm{el}}(E,K)/E=\sum_{q=1}^{N}Z_q^2+2\sum_{q=1}^{N}\sum_{p>q}^{N}Z_qZ_p\langle\Psi_{\mathrm{on}}^{RV}|\cos[\vec{K}\cdot\overrightarrow{R_{qp}}]\times|\Psi_{\mathrm{on}}^{RV}\rangle \tag{4a}$$

with the matrix element in Eq. (4a) understood to be a thermal average over all rovibrational states populated in the initial state, and $\overrightarrow{R_{qp}}$ is the distance between the qth and pth nuclei. It should be noted that $K^2S_{\mathrm{el}}(-1,K)$ is proportional to the area under the quasielastic peak since

TABLE I. The input parameters for calculation of the differential cross sections, sum rules, and centers of gravity of the quasielastic peaks of H_2, D_2, and HD (Refs. 31 and 32).

	Molecule		
	H_2	D_2	HD
Scattering angle θ (deg)	100	100	100
Incident energy (eV)	2250	2250	2250
T (K)	298	298	298
K (a.u.)	19.703	19.703	19.703
M_t (a.u.)	3672	7344	5508
$\frac{K^2}{2M_t}$ (eV)	1.4383	0.7191	0.9589
σ (eV)	0.1840	0.1359	0.1569
R_e (Å)	0.741	0.742	0.741
B_e (eV)	0.007 357 (59.339 cm^{-1})	0.003 708 (29.91 cm^{-1})	0.005 538 (44.667 cm^{-1})
ω_e (eV)	0.5160 (4162.1 cm^{-1})	0.3712 (2994 cm^{-1})	0.4504 (3633 cm^{-1})
D (eV)	4.4779 (36 118 cm^{-1})	4.5560 (36 748 cm^{-1})	4.5136 (36 406 cm^{-1})
x_e	0.028 81	0.020 37	0.024 95
D_e (eV)[a]	5.66×10^{-6}	1.43×10^{-6}	
H_e (eV)[a]	6.06×10^{-9}	8.60×10^{-10}	
α_e (eV)[a]	3.80×10^{-4}	1.34×10^{-4}	

[a] These values were set to zero for all calculations using Eq. (8).

$$\text{Peak area} = \int dE I(E) = N I_0 \int dE \frac{d^2\sigma}{dE d\Omega}(E), \tag{4b}$$

where N is the number density of the target and I_0 is the intensity of the incident electron beam. By employing the definition of the GOS the $S(-1,K)$ sum rule can be written in terms of the peak area as

$$K^2 S(-1,K) = \frac{\text{Peak area}/NI_0}{\left(\frac{d\sigma}{d\Omega}\right)_{\text{Rutherford}}},$$

where

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{Rutherford}} = \frac{1}{K^4}. \tag{4c}$$

In this work we have used the $S_{\text{el}}(0,K)$ sum rule to place relative experimental intensities on an absolute scale. This was considered appropriate since no approximations are made in its derivation other than the assumption that the first Born approximation is valid. The $S_{\text{el}}(-1,K)$ sum rule can then be used as a check on the shape of the measured intensity since only normalization of the correct spectral shape will yield consistent results over multiple sum rules. In the case of theoretical calculations, the sum rule $S_{\text{el}}(-1,K)$ is guaranteed to be satisfied because of the use of normalized distribution functions. Any difference between the sum rule and the value for it obtained from a theoretical calculation is a measure of the numerical accuracy of the intensity calculations. In that case the $S_{\text{el}}(0,K)$ sum rule provides a test of the theoretical prediction. Further points concerning sum rules in the case of diatomic molecules are presented in the supplemental material.[23] We note that the sum rules are linear in the cross section so that such checks can only tell if the shape of the observed signal agrees with theory. Any intensity with the correct shape can be multiplied by an arbitrary constant and the normalization process will then produce correct results for the remaining sum rules.

B. Quasielastic scattering in diatomic molecules

We assume that the first Born approximation holds under the experimental scattering conditions. The exact solution for electron scattering by an atom using a static field representation of the electron density of that atom can be obtained by partial wave calculations.[24] The results of these calculations are normally given in terms of the absolute magnitude of the scattered amplitude and its phase. In the first Born approximation the phase is zero; hence, a nonzero value of the phase represents a failure of the Born approximation. Calculations have shown that although the phase increases in value as K increases, the actual magnitude of the scattered amplitude approaches the first Born value in the limit of large K (see Table I.2B in p. 34 of Ref. 25 for an example). The phase only plays a role in determining the scattering intensity associated with interference scattering between two different nuclei. In the case of nuclei with identical charges, this phase effect should cancel out. The phase does not play a role in atomic scattering. In the following, a theory based on the first Born approximation of scattering theory and incorporating the Born–Oppenheimer approximation will be developed to find out if a conventional quantum mechanical approach can explain the observations reported in Ref. 4.

To evaluate the cross section for quasielastic scattering, it is convenient to approximate the wave functions $\Psi^{TRV}_{\text{on}} = \Phi^{T}_{\text{on}}\Phi^{R}_{\text{on}}\Phi^{V}_{\text{on}}$ and $\Psi^{TRV}_{\text{on}'} = \Phi^{T}_{\text{on}'}\Phi^{R}_{\text{on}'}\Phi^{V}_{\text{on}'}$ as products of translational (T), rotational (R), and vibration (V) wave functions. The sums over n and n' are carried out over all the quantum numbers specifying the three motions (T,R,V).

1. The translational average

Since $e^{i\vec{K}\cdot\overrightarrow{R_{\rm cm}}}\Phi_{\rm on}^{T}$ with $\Phi_{\rm on}^{T}$ a plane wave is an eigenfunction of the translational Hamiltonian, $H_T=-(1/2M_t)\nabla_T^2$, where M_t is the total mass of the molecule, with eigenvalue $(K^2+2\overrightarrow{K}\cdot\vec{P}+P^2)/2M_t$, the translational average can be evaluated using closure over the final translational states. The energy conserving delta function must then be averaged over the initial translational momentum distribution. In the recently reported experiments,[3,4] the target is a gas in thermal equilibrium for which the translational average is

$$\left\langle \delta\left(E-\frac{(K^2+2\vec{K}\cdot\vec{P})}{2M_t}+E_{\rm on}^{RV}-E_{\rm on'}^{RV}\right)\right\rangle=\frac{1}{2\sqrt{\pi}\sigma}e^{-D^2/4\sigma^2},' \tag{5}$$

where

$$D=E-\frac{K^2}{2M_t}+E_{\rm on}^{RV}-E_{\rm on'}^{RV},$$

$$\sigma=\sqrt{\frac{K^2}{2M_t}kT},$$

and where $E_{\rm on}^{RV}$ and $E_{\rm on'}^{RV}$ are the initial and final rovibrational energies of the molecule. Note that the effect of translational motion would be quite different in the case of a molecular beam, as discussed further in the supplemental material.[23] The remaining task is the evaluation of the rovibrational matrices.

2. The rotational average

If K is chosen as the z axis, x as the cosine of the angle K makes with the direction of a unit vector parallel to the bond axis, then $R_1=(\mu/M_1)R$, $R_2=-(\mu/M_2)R$, and $\mu=M_1M_2/(M_1+M_2)$ with R as the instantaneous bond length, then the scattering operator becomes $e^{\pm i(K\mu/M_q)xR}$. The rotational average using the spherical harmonic wave functions $Y_J^M(\theta,\phi)$ is then given as[25]

$$\langle\Phi_{\rm on}^{R}|e^{\pm i(K\mu/M_q)}|\Phi_{\rm on'}^{R}\rangle$$

$$=\frac{1}{2}\sum_{k=0}^{J+J'}(2k+1)\int_{-1}^{1}dtP_k(t)e^{\pm i(K\mu/M_q)Rt}\sqrt{(2J+1)(2J'+1)}\times(-1)^{M'}\begin{pmatrix}J & J' & k\\ M & -M' & 0\end{pmatrix}\begin{pmatrix}J & J' & k\\ 0 & 0 & 0\end{pmatrix}. \tag{6}$$

3. The vibrational average

The vibrational average for harmonic oscillator wave functions has been given previously.[15] Equation (C6) in Ref. 15 can be used with the Bessel function, $I_l(x)$, replaced by the first term in its expansion as $I_l(x)=x^l/2^l l!$. This approximation is good to better than 0.1% for values of the argument less than 0.01. The Morse model is used to describe the anharmonic vibrational motion since it is considered to be more realistic. A previous treatment for CH_4 (Ref. 3) indicated that the harmonic case is very similar for hydrogen stretching modes, as long as higher vibrational states do not contribute. The solutions of the Schrödinger equation for the Morse potential, $U(R)=D(1-e^{-a(R-R_e)})^2$ are[25]

$$\Phi_v^{\rm Morse}(z)=\sqrt{\frac{v!}{\Gamma(v+b[v]+1)}}e^{-(z/2)}z^{(b[v]/2)}L_v^{b[v]}(z), \tag{7}$$

where $z=2de^{-a(R-R_e)}$, $L_v^{b[v]}(z)$ is a Laguerre function, R_e is the equilibrium bond length, D is the dissociation energy, a is a constant given as $a=\omega_e\sqrt{\mu/2D}$, while $d=1/a\sqrt{2\mu D}=2D/\omega_e$ where ω_e is the vibrational frequency. Strictly speaking, both d and $b[v]$ are also functions of the rotational energy [Ref. 25—Eqs. (1)–(3), (4a)–(4c), and (5)–(15)] which has been neglected in this treatment. The constant $b[v]$ is defined as

$$b[v]=\left(\frac{2}{a}\right)\sqrt{\frac{2\mu(D-E[v])}{d}}$$

with the vibrational energy $E[v]$ defined as

$$E[v]=\omega_e\left(v+\tfrac{1}{2}\right)\left[1-x_e\left(v+\tfrac{1}{2}\right)\right].$$

For the Morse oscillator only the constants ω_e and D are independent parameters and can be set equal to experimental values. The parameter x_e is defined in terms of these as $x_e=\omega_e/4D$. The effect of vibration-rotation coupling on the vibrational wave function is small for the low-lying vibrational levels that are excited. Hence the dependence of d and $b[v]$ on J will be neglected.

Because the Morse solutions are orthogonal only if $b[v]$ is a constant independent of v, a set of orthogonal anharmonic wave functions, $\Phi_v^{\perp}(z)$, was constructed from the Morse functions. These orthogonal functions performed much better at satisfying the sum rules and yield eigenvalues identical to those of the Morse functions with the same value of v. The expression for the cross section using these functions can be written as

$$K^4\frac{d^2\sigma}{dEd\Omega}=\frac{1}{2N\sqrt{\pi}\sigma}\sum_{J=0}^{J_{\rm max}}(2J+1)\sum_{v=0}^{v_{\rm max}}e^{-E(J,v)/kT}\sum_{J'=0}^{J_{\rm max}}(2J'+1)\sum_{k=0}^{2J_{\rm max}}(2k+1)\begin{pmatrix}J & J' & k\\ 0 & 0 & 0\end{pmatrix}^2\sum_{v'=0}^{v_{\rm max}}e^{-(E-K^2/2M_t+E(J,v)-E(J',v'))^2/4\sigma^2}\times\left|\int_0^{\infty}dz\left\{\sum_{q=1}^{2}Z_q^{\rm eff}j_k\left[\frac{K\mu R_e}{M_q}\left(1-\frac{1}{aR_e}\ln\left[\frac{z}{2d}\right]\right)\right]\right\}\Phi_v^{\perp}(z)\Phi_{v'}^{\perp}(z)\right|^2 \tag{8}$$

with

$$N = \varepsilon \sum_{J=0}^{J_{\max}} (2J+1) \sum_{v=0}^{v_{\max}} e^{-E(J,v)/kT}, \tag{9}$$

where ε is one for heteronuclear diatomics and $\frac{1}{2}$ for homonuclear diatomics.

Here

$$E(J,v) = B_e J(J+1) - D_e J^2(J+1)^2 + H_e J^3(J+1)^3 - \alpha_e J(J+1)\left(v+\tfrac{1}{2}\right) + \omega_e\left(v+\tfrac{1}{2}\right)\left[1 - x_e\left(v+\tfrac{1}{2}\right)\right], \tag{10}$$

where B_e is the rotational constant, D_e and H_e are centrifugal distortion constants, and α_e is the rotation-vibration interaction constant. Note that the terms involving D_e, H_e, and α_e are neglected in the calculation of the cross sections but were included in the calculation of the concentrations of ortho-para isomers as a function of temperature using Eqs. (11) and (12) as discussed in Sec. III.

III. RESULTS AND DISCUSSION

A. Calculation of quasielastic scattering for HD, H_2, and D_2

The heteronuclear case, HD, has been calculated by numerically evaluating Eq. (8). The homonuclear case is complicated by symmetry requirements on the wave functions imposed by the presence of identical nuclei. The hydrogen nucleus has a spin of $\pm\frac{1}{2}(\alpha=\frac{1}{2},\beta=-\frac{1}{2})$, which gives rise to the symmetric nuclear spin wave functions $\alpha(1)\alpha(2)$, $\beta(1)\beta(2)$, and $1/\sqrt{2}(\alpha(1)\beta(2)+\beta(1)\alpha(2))$ and the antisymmetric function $1/\sqrt{2}(\alpha(1)\beta(2)-\beta(1)\alpha(2))$. The molecular rotational wave functions can be written in terms of spherical harmonics, $Y_J^M(\theta,\phi)$, in both a symmetric and an antisymmetric form with respect to interchanging the two nuclei as $\frac{1}{2}[Y_J^M(\theta,\phi)+(-1)^J Y_J^M(\theta,\phi)]=Y_{2n}^M(\theta,\phi)$ and $\frac{1}{2}[Y_J^M(\theta,\phi)-(-1)^J Y_J^M(\theta,\phi)]=Y_{2n+1}^M(\theta,\phi)$. Since half-integer spins follow Fermi–Dirac (FD) statistics the allowed wave functions for H_2 must be antisymmetric with respect to nuclear interchange. This leads to three states with $J=2n+1$, called orthohydrogen and one state with $J=2n$, called parahydrogen.

In the case of D_2 each deuteride has integer spin states +1, 0, −1 which leads to nine molecular nuclear spin states of which six are symmetric and three are antisymmetric. Since the nuclear spin is integer the D_2 wave function must obey Bose–Einstein (BE) statistics so there are six states with $J=2n$ ("ortho" deuterium—symmetric nuclear spin wave functions), and six states with $J=2n+1$ ("para" deuterium—antisymmetric nuclear spin wave functions).

The fractions of para and ortho forms present in each species are given by

$$N_p = \frac{\eta_p}{N} \sum_{J=0}^{J_{\max}} (4J+1) \sum_{v=0}^{v_{\max}} e^{-E(2J,v)/kT} \tag{11}$$

and

$$N_o = \frac{\eta_o}{N} \sum_{J=0}^{J_{\max}} (4J+3) \sum_{v=0}^{v_{\max}} e^{-E(2J+1,v)/kT} \tag{12}$$

with N given by Eq. (9). The cross section for an equimolar mixture of the ortho and para forms in thermal equilibrium can be written as

$$K^4\left(\frac{d^2\sigma}{dEd\Omega}\right)_{\text{mixture}} = \eta_p K^4\left(\frac{d^2\sigma}{dEd\Omega}\right)_p + \eta_o K^4\left(\frac{d^2\sigma}{dEd\Omega}\right)_o \tag{13}$$

with $\eta_p=\frac{1}{4}(H_2)$ or $\frac{2}{3}(D_2)$ and $\eta_o=\frac{3}{4}(H_2)$ or $\frac{1}{3}(D_2)$. Here $K^4(d^2\sigma/dEd\Omega)_p$ is given by Eq. (8) with the sums over J and J' limited to even values while for $K^4(d^2\sigma/dEd\Omega)_o$ the same sums are limited to odd values of J and J'.

A script written in MATHEMATICA™ (Wolfram Research), which contains all the molecular parameters and computes the quasielastic scattering signals and the associated sum rule values, is provided as a part of the supplemental material.[23]

B. Comparison of calculated and experimental quasielastic spectra

Figure 1 plots the experimental quasielastic scattering spectra of H_2, D_2, HD, and the 50:50 H_2:D_2 mixture reported earlier.[4] Note that the experimental spectra are now presented on an absolute oscillator strength scale since the original relative intensities were made absolute by normalization to the $S(0,K)$ sum rule. In order to compare the computed and experimental spectra, it is necessary to convolute the computed spectra with the energy resolution of the experiment. The experimentally measured energy resolution, expressed as full width at half maximum height (FWHM), was obtained by a least-squares fit of the elastic scattering spectrum of Ar (Ref. 26) and found to be 0.80 ± 0.06 eV assuming a Gaussian shape.

The experimental spectra were placed on an absolute scale by normalizing them to the theoretical value of the $S(0,K)$ sum rule using a least-squares procedure in which the value of

$$F_{\text{LS}} = \frac{\sqrt{\dfrac{\sum_{n=1}^{N}\left[\dfrac{d^2\sigma}{dEd\Omega}(E_n,K)_{\text{expt}} - \dfrac{d^2\sigma}{dEd\Omega}(E_n,K)_{\text{theory}}\right]^2}{N-1}}}{\left(\dfrac{d^2\sigma}{dEd\Omega}\right)_{\max}} \tag{14}$$

was minimized with respect to the choice of energy resolution. The average value of the optimized molecular resolution factors was 0.80 ± 0.02 eV, which was the value used in the final calculation of the sum rules. In the comparisons that follow, it was assumed that the uncertainty in the determination of the zero of the energy loss scale was ±0.05 eV (note that an uncertainty of 1° in the scattering angle corresponds to a 0.04 eV shift in the energy scale) and that the

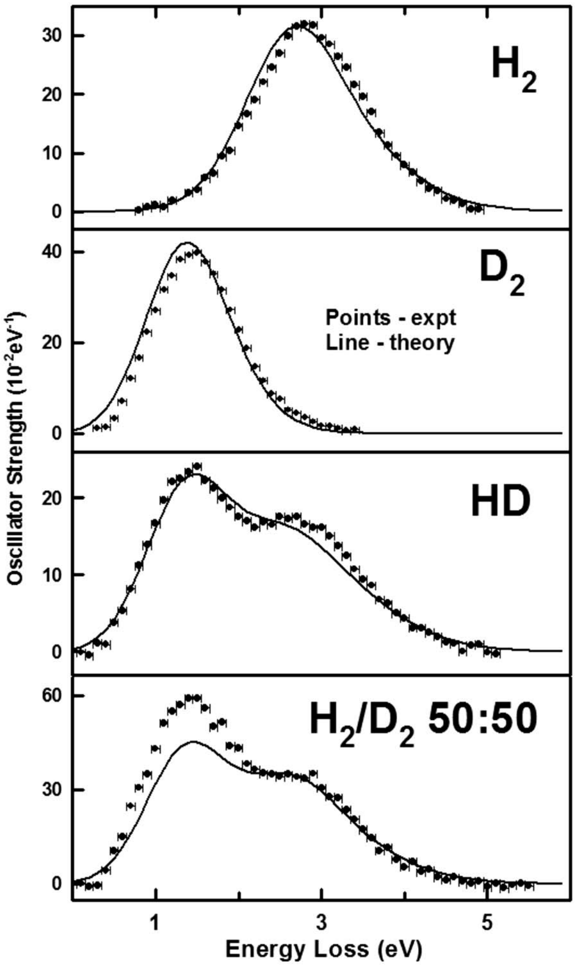

FIG. 1. The experimental quasielastic scattering spectra (Ref. 4) of H_2, D_2, HD, and a 50:50 mixture of H_2 and D_2 (circles and error bars) compared to predictions of the present theory (solid line). The computed cross sections are absolute. The intensity scales for the experimental data were established by using the $K^2S(0,K)$ sum rule to normalize the experimentally determined relative intensities.

uncertainty in the normalized cross section was given by the square root of the number of counts in each data point normalized to the absolute intensity scale. This uncertainty can be written as

$$\Delta \frac{d^2\sigma}{dEd\Omega}(E_n,K)_{\text{expt}} = \sqrt{\frac{\frac{d^2\sigma}{dEd\Omega}(E_n,K)_{\text{expt}}\frac{d^2\sigma}{dEd\Omega}(E_n,K)_{\text{max}}}{N_{\text{max}}}}, \tag{15}$$

where N_{max} is the number of counts in $d^2\sigma/dEd\Omega(E_n,K)_{\text{max}}$, the value of the cross section at the peak maximum.

In order to determine the effect of anharmonicity on the quasielastic scattering, calculations were carried out for H_2 for the harmonic oscillator and orthogonalized Morse cases. It was found that the two results were effectively identical, as was noted earlier for the case of CH_4.[2] This is because only the first few vibrational states make significant contributions to the quasielastic scattering.

The results of this calculation for quasielastic scattering by H_2, D_2, and HD are compared to the experimental signals in Fig. 1. The theoretical results were broadened with a Gaussian of 0.8 eV FWHM. The parameters used in the calculations are given in Table I. Table II presents the results for the sum rules and the energy of the center of gravity of the quasielastic peak for the three molecules. The least-squares fit result F_{LS} [Eq. (14)] is given in Table II for each molecule. It was also determined that the *TRV* temperatures of the molecules in this study were all within 20° of 298 K by varying the temperature in Eq. (13) until disagreement between the shape of theory and experiment exceeded the experimental uncertainty. Note that at this temperature, nuclear spin effects do not play a role in the value of the sum of the ortho plus para isomers given by Eq. (13). The FD and BE statistical weightings are still considered in calculating the intensities but the cross sections before multiplication by the spin weights are the same for both molecules within the experimental uncertainties. In constructing the computed spectra, the theoretical nuclear spin isomer cross sections without the nuclear spin weights are about half the total since odd-even and even-odd rotational transitions are forbidden.

The fourth panel of Fig. 1 shows the experimental result for a 50:50 mixture of H_2 and D_2 compared to the sum of the theoretical cross sections for H_2 and D_2. The experimental spectrum of the 50:50 $H_2:D_2$ mixture was normalized using the same procedure as that applied to the spectra of the pure

TABLE II. Calculated and observed sum rules and center of gravity energies (E_{cg}) of the quasielastic electron scattering peaks from H_2, D_2, and HD.

	H_2		D_2		HD	
	Theory	Expt.	Theory	Expt.	Theory	Expt.
$K^2S(-1,K)$ [a]	2.0000	1.9984	2.0000	2.0014	2.0000	2.0005
$S(0,K)$ [a]	0.2114	0.2104	0.1057	0.1061	0.1586	0.1559
E_{cg} (eV)	2.8766	2.90(4)	1.4351	1.53(4)	2.1432	2.18(4)
$K^2S_p(-1,K)$	2.0020		2.0014		0.5104[b]	
$S_p(0,K)$	0.2108		01061			
$K^2S_o(-1,K)$	1.9922		2.0014		0.5102[c]	
$S_o(0,K)$	02 094		0.1061			
F_{LS}		0.040		0.065		0.043

[a] These sum rules ignore nuclear spin effects.
[b] Sums over J and J' are over even values only.
[c] Sums over J and J' are over odd values only.

TABLE III. Calculated percent of the total peak area and contribution to the position of the center of gravity of the peak due to various excitation types in quasielastic electron scattering from H_2, D_2, and HD.

	Peak area			Peak center of gravity		
	T	$R+T$, $v=0$	$R+T$, $v\neq 0$	T	$R+T$, $v=0$	$R+T$, $v\neq 0$
H_2	0.05	52	48	50	41.5	8.5
D_2	0.08	61	39	50	40	10
HD	0.01	58	42	44.4	39	16.6

molecules. The anomalous nature of the experimental quasielastic cross section of the 50:50 $H_2:D_2$ mixture is clear. Note that this H_2/D_2 intensity anomaly does not show up in the spectral plots of the pure H_2 and D_2 since those spectra are independently sum rule normalized—it is necessary to perform a simultaneous measurement of H_2 and D_2 in a 50:50 mixture in order to observe the effect. Also note that the argument presented here does not depend on the results for the HD molecule.

If the ortho-para sum rules for $S(-1,K)$ are multiplied by their nuclear spin weights and added together then the ratio of the resulting deuterium to hydrogen molecular cross sections for an equimolar mixture is 1.0018, which is in good agreement with the predictions of Eqs. (11) and (12) for a temperature of 298 K.

For pure H_2 (top panel of Fig. 1), the calculated peak shape is in good agreement with experiment, although a better fit could be obtained by shifting the calculated result to higher energy loss by 0.02 eV. For D_2 the shape of the calculated peak is also in good agreement with experiment but there is a shift of about 0.09 eV to lower energy loss relative to experiment, which is almost twice the uncertainty in the energy loss scale.

For HD the center of gravity of the calculated peak is 0.03 eV lower than the experimental value, which is within the estimated uncertainty in the energy loss scale of ±0.05 eV. Note that the separate sums over even J and odd J values only yield about a quarter of the area contribution, unlike for the hydrogen and deuterium molecules since there are no nuclear spin restrictions on transitions in HD. Also note that for HD the average translational energy transferred to the molecule, $K^2/(2M_t)$, is no longer half the total energy transfer.

In addition to the results presented above, calculations were carried out for $T=5$ K for H_2. The results for the sums of the intensities of the even J and odd J cross sections, neglecting the spin weights (i.e., the cross section if nuclear spin effects are neglected) showed that the sum rules were independent of temperature. Of course the separate J even and J odd sums behave very differently with temperature since at absolute zero only the $J=0$ even state is populated.

Each rovibrational transition occurs at the translational energy loss of $K^2/2M_t$ plus the rovibrational excitation energy. It was observed computationally that the most probable excitation was to $\Delta J=12$ for $\Delta v=0$ with the selection rule $\Delta J=2n$. As Δv increased the J value for the most probable excitation decreased. For $\Delta v=1$ the most probable excitation occurred at $\Delta J=10$. It also proved possible to dissect the sum rules and peak positions into contributions from the various excitation modes. These results are summarized in Table III and the contributions to the quasielastic scattering from H_2 from pure-T, $(T+R)$ for $v=0$, and $(T+R)$ for $v>0$ at 300 K are plotted in Fig. 2. For all three molecules (translation +rotation) without vibrational excitation contributes over half the intensity. While the rovibrational excitation with $v=1$ is the largest single vibrational contribution, there is a significant vibrational excitation up to $v=8$ since increasing $v_{\max}$ from 7 to 8 makes a detectable change in the line shape and total intensity. Depending on the species, vibrational excitation (accompanied by $T+R$) contributes from 39% to 48% of the total intensity.

It is interesting to consider what would be the result if the ortho and para subpopulations of H_2 and D_2 were not those at thermal equilibrium, but rather that their relative abundance was that of a much lower temperature. The calculated temperature dependence of the ratio of the intensities of the quasielastic scattering signal for D_2 to that for H_2 is presented in Fig. 3. This result was obtained using Eqs. (8)–(12) with all the parameters in Table I used in the energy expression and with D_e, H_e, and α_e set to zero. A temperature of 82 K is required for a 30% anomaly in the deuterium to hydrogen ratio (such as was seen experimentally in the 50:50 H_2/D_2 mixture—see bottom panel in Fig. 1) for the full expression for the energy, and 85 K with the neglect of D_e, H_e, and α_e. The small difference between these two results justifies the use of the simpler form for the rovibration energy in the calculation of the cross sections. It is clear from Fig. 2 that major changes in this ratio do not occur above 200 K. Of interest in this regard, it is known[27] that ortho-para-H_2 mix-

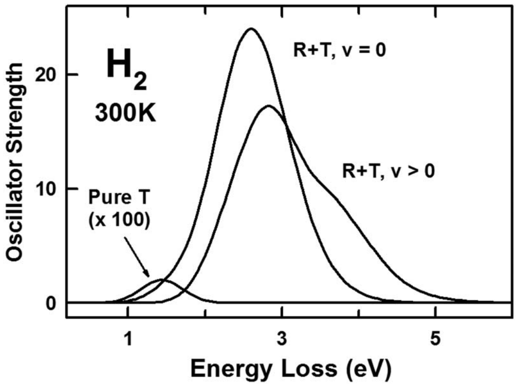

FIG. 2. Decomposition of the calculated quasielastic scattering signal for H_2 at 300 K into separate contributions of (i) pure translational (negligible), (ii) (translation+rotation) without vibrational excitation, and (iii) (translation +rotation) with vibrational excitation. The theoretical curves were convoluted with 0.05 eV FWHM Gaussians to represent experimental broadening of possible high resolution experiments.

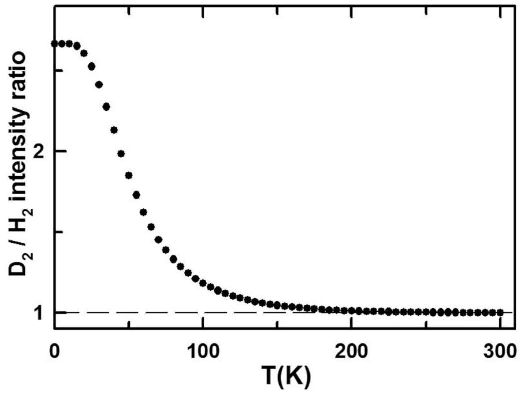

FIG. 3. The temperature dependence of the ratio of the intensity of quasielastic scattering from D_2 relative to that for H_2 in an equimolar mixture, at equilibrium, given by Eq. (13). The input parameters used in the calculation are listed in Table I and were taken from Refs. 31 and 32. The variation is related to the temperature dependence of the ortho-para equilibrium, and the difference in the ortho and para contributions to the rotational fine structure.

tures equilibrated at lower temperatures can be heated to higher temperatures in the absence of a paramagnetic catalyst without altering the ortho to para ratio established at the lower temperature. Astronomers are familiar with situations where the ortho-para ratio of molecular hydrogen is that for 90 K, while the actual temperature of the gas (T,R,V) is 600 K.[28,29] However, it is also worth noting that identical quasielastic electron energy loss spectra were obtained from two separate samples of the 50:50 H_2/D_2 mixture that were stored for extended periods at ~10 atm in regular steel lecture bottles, conditions where the ortho-para equilibrium is established rapidly.[30] It is therefore highly unlikely that there would be any nonthermal equilibrium of ortho-/para-H_2 in the experimental samples.

Figure 4 plots the calculated quasielastic spectra for H_2 at $T=5$, 70, and 300 K, broadened with a Gaussian of 50 meV FWHM, with display of the individual contributions from the ortho and para nuclear spin isomers, assuming the thermal equilibrium population. At lower temperatures where the translational broadening is negligible, it would be possible to resolve individual rovibrational contributions if a spectrometer having 50 meV FWHM energy resolution was used. Spectra at that energy resolution could readily determine if the ortho/para populations were at thermal equilibrium. Experimentally measuring quasielastic scattering spectra with 50 meV resolution would be quite difficult owing to the very low cross section—the experimental spectra typically take a few weeks to record with our unmonochromated spectrometer, which has relatively efficient lenses and a parallel detector that increases throughput by a factor of ~30 relative to a single channel detector. However such measurements could be done if there was sufficient interest.

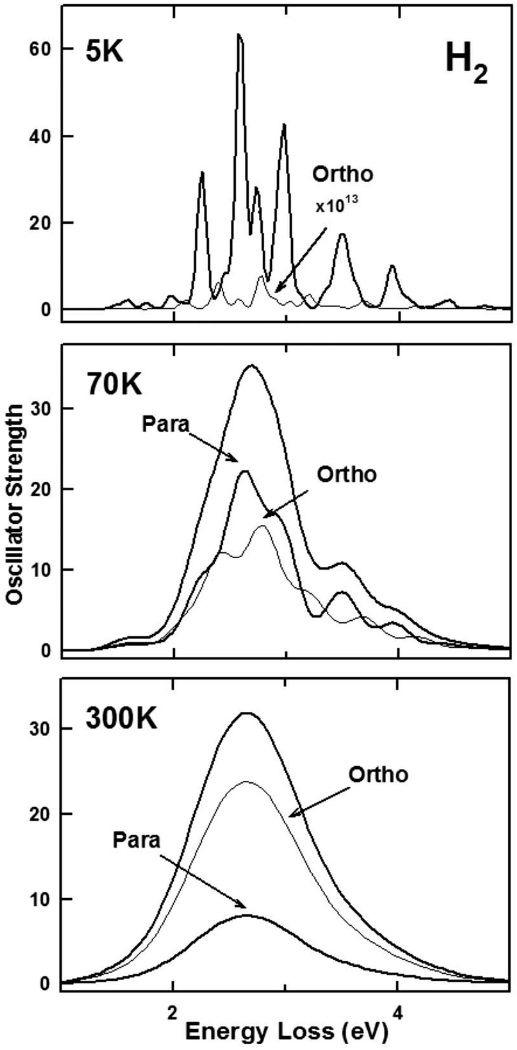

FIG. 4. The calculated quasielastic scattering spectrum of H_2 with decomposition into the contributions from ortho and para nuclear spin isomers at temperatures of 5, 70, and 300 K. Convolution with Gaussians of 50 meV FWHM was performed in order to show expected results from possible high resolution experiments.

IV. CONCLUSIONS

Without assuming the Rutherford model, we have computed the expected signals for quasielastic scattering by H_2, D_2, and HD at a large momentum transfer but at energy transfer values below the dissociation threshold. No assumptions were made about any spectroscopic selection rules, reasonable approximations were employed for all the molecular wave functions involved, and nuclear spin statistics issues were fully taken into account. We find that the first Born approximation treatment with an anharmonic description of vibration provides a good description of the observed experimental peak shapes for quasielastic scattering for H_2, D_2, and HD. The peak positions are in good agreement with theory. However, the present theoretical approach cannot explain the experimental observations[4] that the intensity ratio of the H and D quasielastic scattering peaks from an equimolar mixture of D_2 and H_2 deviates from that for the H and D peaks in HD by 31(4)%.[4] This puzzle remains to be solved.

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