

## Role of Boson-Fermion Statistics on the Raman Spectra of $\text{Br}_2(X)$ in Helium Clusters

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The role played by the bosonic or fermionic character of He atoms surrounding a  $\text{Br}_2(X)$  molecule is analyzed through vibrotational Raman spectra simulations. Quantum chemistry-type calculations reveal the spin multiplicity to be chiefly responsible for the drastic difference observed by Grebenev *et al.* [Science **279**, 2083 (1998)] in the rotational structure of molecules embedded in helium droplets.

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A marked difference was observed in the infrared (IR) spectra of an oxygen carbon sulfide (OCS) molecule surrounded by helium atoms depending on their isotopic form [1]. For  $^4\text{He}$ , the spectrum resembled that of isolated OCS with well-defined *P* and *R* branches, while for  $^3\text{He}$  the spectrum became highly unstructured, showing a rather broad band. The addition of 60  $^4\text{He}$  atoms to a  $^3\text{He}$  droplet restored the structure of the spectrum, suggesting an almost freely rotating OCS. These results were interpreted as a microscopic manifestation of superfluidity of  $^4\text{He}$  at low temperatures [1].

Previous theoretical studies have mainly focused on the structure of the He droplets around atoms or molecules using different methodologies, such as variational [2], diffusion [3], and path integral [4,5] Monte Carlo calculations, as well as density functional theory calculations [6]. However, as far as we know, no attempts have been made to simulate spectra of molecules embedded in He clusters apart from earlier work showing larger widths of molecular rotational levels in fermionic helium liquids than in bosonic ones [7]. Quantum chemistry methodology was indeed used for the first time [8] to study small  $^3\text{He}_N$  complexes ( $N = 1, 2$ ) bound to an atomic or molecular impurity. One of the interests of such an approach is that the wave functions supplied by it can be used to perform simulations of spectra.

Along similar lines, we study here fermionic, bosonic, and mixed He clusters doped with one  $\text{Br}_2(X)$  diatomic molecule. To treat the different cases on the same footing, Hartree and Hartree-Fock calculations are performed within an adiabatic separation of diatomic vibrations. This allows us to establish the role played by the bosonic or fermionic character of the surrounding He atoms through simulated Raman spectra.

Using satellite coordinates  $(\mathbf{r}, \mathbf{R}_k)$ , where  $\mathbf{r}$  is the vector joining the two bromine atoms,  $\mathbf{R}_k$  are the vectors

connecting the diatomic center of mass with the different helium atoms, and, neglecting kinetic couplings, the Hamiltonian for the entire system can be approximated as

$$H = h(r, \mathbf{j}) + \sum_{k=1}^N h_k^{(\epsilon)}(\mathbf{R}_k, r) + \sum_{k<l} V_{kl}(|\mathbf{R}_k - \mathbf{R}_l|). \quad (1)$$

It consists of a diatomic part

$$h(r, \mathbf{j}) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} + U(r) + \frac{\mathbf{j}^2}{2mr^2}, \quad (2)$$

three-atom Hamiltonians for  $N$  He- $\text{Br}_2$  subsystems

$$h_k^{(\epsilon)}(\mathbf{R}_k, r) = -\frac{\hbar^2}{2\mu_\epsilon} \frac{\partial^2}{\partial R_k^2} + \frac{\mathbf{l}_k^2}{2\mu_\epsilon R_k^2} + W(r, R_k, \theta_k), \quad (3)$$

and  $\binom{N}{2}$  He-He interactions,  $V_{kl}$ . Here,  $m$  is the diatomic reduced mass,  $\mathbf{j}$  is the angular momentum associated with  $\mathbf{r}$ ,  $U$  is the intramolecular diatomic potential,  $\mu_\epsilon$  is the reduced  $^\epsilon\text{He}-\text{Br}_2$  mass ( $\epsilon = 3, 4$ ),  $\mathbf{l}_k$  is the angular momentum associated with  $\mathbf{R}_k$ , and  $W$  is the weak atom-diatom potential that depends on the  $(r, R_k)$  distances and the angle  $\theta_k$  formed by the  $\mathbf{r}$  and  $\mathbf{R}_k$  vectors. Choosing a body-fixed (BF) coordinate system with the *Z* axis parallel to  $\mathbf{r}$ , we resort to an adiabatic approximation used earlier to calculate vibrational frequency shifts [9]. At different values of  $r$ , one seeks the ground state by solving the Schrödinger equation

$$\left[ \sum_{k=1}^N h_k^{(\epsilon)} + \sum_{k<l} V_{kl} - E_{\Lambda,S}^{(N)}(r) \right] \Phi_{\Lambda,S}^{(N)}(\{\mathbf{R}_k\}; r) = 0 \quad (4)$$

through Hartree or Hartree-Fock methodology depending on the statistics obeyed by the helium adatoms. In (4), the  $r$ -dependent eigenenergies are labeled by  $\Lambda$ , the projection of the orbital angular momentum  $\mathbf{L} = \sum_{k=1}^N \mathbf{l}_k$  on

$\mathbf{r}$ , and the total spin  $S$ . These levels, which for bosons correspond to  $S = \Lambda = 0$  states, are degenerate with respect to the spin projection  $\Sigma$ . For a total angular momentum  $\mathbf{J} = \mathbf{j} + \mathbf{L} + \mathbf{S}$ , with projection onto the BF  $Z$  axis  $\Omega = \Lambda + \Sigma$ , the states of the “modified” diatom,  $\chi_{J\Lambda\Sigma\nu}$ , are eigenstates of an *effective* Hamiltonian

$$H_N^{\text{eff}} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} + U(r) + E_{\Lambda,S}^{(N)}(r) + \frac{\hbar^2}{2mr^2} G \quad (5)$$

with eigenenergies  $\varepsilon_{J\Lambda\Sigma\nu}$ , where  $\nu$  is the stretching quantum number and where, neglecting Coriolis couplings,

$$G = J(J+1) + \bar{L}(\bar{L}+1) + S(S+1) - 2(\Lambda^2 + \Sigma^2 + \Lambda\Sigma). \quad (6)$$

Since the orbital angular momentum is here not a good quantum number, an average  $\langle \Phi_{\Lambda,S}^{(N)} | \mathbf{L}^2 | \Phi_{\Lambda,S}^{(N)} \rangle \approx \hbar^2 \bar{L}(\bar{L}+1)$  estimated at the equilibrium distance  $r_{\text{eq}}$  has been accounted for. So, within this approximation, the total wave function becomes

$$\Psi \approx \mathcal{D}_{M\Omega}^J(\varphi_r, \theta_r, 0) \Phi_{\Lambda,S}^{(N)}(\{\mathbf{R}_k\}; r) \chi_{J\Lambda\Sigma\nu}(r), \quad (7)$$

where  $\mathcal{D}_{M\Omega}^J$  are Wigner rotation matrices depending on the angular polar components  $(\theta_r, \varphi_r)$  of  $\mathbf{r}$  in a space-fixed (SF) frame.

To deal with  $N$  fermion/ $M$  boson mixtures, we use a “self-consistent field” treatment [10] in which the wave function is expressed as a product  $\Phi_{\Lambda,S}^{(N)} \Phi_{0,0}^{(M)}$ . Starting with the solution of Eq. (4) for pure fermions, the corresponding wave function is used to average the potential coming from fermion-boson interactions,  $V_{F/B} = \sum_{k=1}^N \sum_{l=1}^M V_{kl}(|\mathbf{R}_k - \mathbf{R}_l|)$ . This is included as an additional term in Eq. (4) for solving the “perturbed”  $M$ -boson system. In turn, the resulting bosonic wave function is used to average  $V_{F/B}$  again, then solve for the perturbed  $N$  fermion system, with the whole process iterated to convergence.

To solve Eq. (4) for a pure fermionic cluster of size  $N$  and spin  $S$ , the nuclear wave function is described as a Slater determinant of one-fermion spin orbitals, whose spatial part is determined by means of restricted closed-shell or open-shell Hartree-Fock approaches through a direct minimization procedure [11] to force convergence to the global minimum. For boson clusters, the wave function is a Hartree product in which all the particles occupy the same orbital. For bosons and singlet fermions, and starting from  $N = 2$ , the initial orbitals are those corresponding to independent particles. For larger  $N$  values the chosen initial orbitals were those obtained from the preceding calculation with  $N - 2$  particles. For  $S \neq 0$  fermions, one starts with the optimized orbitals from the  $S - 1$  calculation for the same size cluster. In either case, spatial one-particle orbitals are expanded in terms of products of radial functions and spherical harmonics,  $g_n(R; r) Y_{lm}(\theta, \phi)$ . At each  $r$  value, the  $g$  func-

tions are obtained by Schmidt orthogonalization of the set of ground states corresponding to the triatomic system  ${}^e\text{He-Br}_2$  at  $n_{\text{max}}$  fixed orientations,  $\theta$ , equally spaced in  $[0, \pi/2]$ .

Let us consider a Raman scattering

$$\text{Br}_2 \cdots \text{He}_N(i) + \hbar\omega_0 \rightarrow \text{Br}_2 \cdots \text{He}_N(f) + \hbar\omega_{fi}, \quad (8)$$

where  $\omega_0$  and  $\omega_{fi}$  are the incident and exiting photon frequencies, respectively, while the system evolves from an initial  $i$  to a final state  $f$ . We consider linear polarized incident light, whose electric vector  $\hat{\mathbf{e}}$  defines the SF  $Z$  direction, propagating along the  $Y$  axis. The scattered light is detected along the  $X$  axis. In terms of the diatomic polarizability diagonal matrix in BF  $\boldsymbol{\alpha}$ , assumed to be unaffected by complexation, matrix elements of the spherical components of the induced dipole moment  $\boldsymbol{\mu} = \boldsymbol{\alpha}\hat{\mathbf{e}}$  between  $i$  and  $f$  states of type (7),  $\mu_k^{f,i} = \langle \Psi_f | \mu_k | \Psi_i \rangle$ , conserving  $\Lambda$  and  $S$ , become

$$\begin{aligned} \mu_k^{f,i} &\sim (-1)^{M_i} \sum_{m,n} (-1)^m \alpha_m^{f,i} (2n+1) \\ &\times \begin{pmatrix} 1 & 1 & n \\ -m & m & 0 \end{pmatrix} \begin{pmatrix} 1 & 1 & n \\ -k & 0 & k \end{pmatrix} \begin{pmatrix} J_i & n & J_f \\ -M_i & 0 & M_i \end{pmatrix} \\ &\times \begin{pmatrix} J_i & n & J_f \\ -\Omega_i & -k & \Omega_f \end{pmatrix}, \end{aligned} \quad (9)$$

where  $\alpha_m^{f,i} = \langle \chi_{J_f S_f \Omega_f \nu_f} | \alpha_m | \chi_{J_i S_i \Omega_i \nu_i} \rangle$ . For bosons ( $\Omega_i = \Omega_f = 0$ ), only  $\mu_0$  survives and the scattered light emerges polarized along  $Z$  (parallel signal), leading to standard diatomic-type selection rules  $\Delta J = 0, \pm 2$ , contributing to  $Q$ ,  $S$ , and  $O$  branches. To stress the difference between boson/fermion environments, detection along the  $X$  axis for linear parallel polarization is considered. In terms of the spherical and anisotropic parts of the polarizability [12],  $\alpha_{f,i} = (\alpha_0^{f,i} + 2\alpha_1^{f,i})/3$  and  $\beta_{f,i}^2 = (\alpha_0^{f,i} - \alpha_1^{f,i})^2$ , respectively, one finds

$$\begin{aligned} \mu_0^{f,i} &\sim \alpha_{f,i} \begin{pmatrix} J_i & 0 & J_i \\ -M_i & 0 & M_i \end{pmatrix} \begin{pmatrix} J_i & 0 & J_i \\ -\Omega_i & 0 & \Omega_i \end{pmatrix} \\ &+ \frac{2\beta_{f,i}^2}{3} \begin{pmatrix} J_i & 2 & J_f \\ -M_i & 0 & M_i \end{pmatrix} \begin{pmatrix} J_i & 2 & J_f \\ -\Omega_i & 0 & \Omega_i \end{pmatrix} \end{aligned} \quad (10)$$

conserving the third component of  $J$  in SF and BF frames. So, there is a remarkable difference for complexes containing fermions with  $\Omega_i \neq 0$ , since transitions with  $\Delta J = \pm 1$  become allowed and, thus,  $P$  and  $R$  branches should appear in the spectrum. Considering a Boltzmann distribution over cluster states at a given temperature  $T$  and averaging over initial rotational states, a line of intensity

$$I_{fi}(T) \propto \frac{e^{-(\varepsilon_i/kT)}}{\sum_i e^{-(\varepsilon_i/kT)}} \frac{1}{2J_i + 1} \sum_{M_i} |\mu_0^{f,i}|^2 \quad (11)$$

would appear at an energy  $\hbar\omega_{fi} = \hbar\omega_0 - (\varepsilon_f - \varepsilon_i)$  of the scattered photon. To get continuum profiles, we consider a diatomic ( $\nu = 1 \leftarrow 0$ ) transition enabling the breaking up of the complex via vibrational predissociation (VP). The corresponding VP width,  $\Gamma$ , is then used for dressing the above lines with Lorentzian functions. Summing over transitions, a continuum spectrum is then obtained,

$$\sigma(\omega; T) = \sum_{f,i} \frac{\Gamma_{fi}/2\pi}{\hbar^2(\omega - \omega_{fi})^2 + \Gamma_{fi}^2/4} I_{fi}(T), \quad (12)$$

fulfilling the condition  $\int d\omega \sigma(\omega; T) = \sum_{f,i} I_{fi}(T)$ . A crude estimation of VP widths, depending on size and character, is attained. Energies  $E^{(1)}$  and angular-dependent VP rates  $\Gamma_{fi}(\theta)$  for triatomic  $^3\text{He}$ - and  $^4\text{He}$ - $\text{Br}_2$  species are first obtained [13]. Size-dependent angular densities  $\mathcal{D}^{(N)}(\theta)$ , obtained by squaring the  $\Phi_{\Lambda,S}^{(N)}$  functions and integrating over all the variables but one, are then used to average  $\Gamma_{fi}(\theta)$ . Finally, they are multiplied by the number of effective bonds  $N^{\text{eff}} = E_{\Lambda,S}^{(N)}(r_{\text{eq}})/E^{(1)}$ . For a  $N$  fermion/ $M$  boson mixture, the coupling term  $\langle V_{F/B} \rangle$  is democratically shared between the two components, getting a new effective number of bonds  $\mathcal{N} = [E_{\Lambda,S}^{(N)}(r_{\text{eq}}) + \frac{N}{M+N}\langle V_{F/B} \rangle]/E^{(1)}$  for fermions, and similarly for bosons,  $\mathcal{M}$ . So, the VP rate becomes  $\Gamma_{fi}^{(N/M)} = \frac{\mathcal{N}}{N^{\text{eff}}} \Gamma_{fi}^{(N)} + \frac{\mathcal{M}}{M^{\text{eff}}} \Gamma_{fi}^{(M)}$ .

The  $\text{Br}_2(X)$  interaction  $U$  is described by a Morse function [14], while the  $\text{He-Br}_2(X)$  potential  $W$  is approximated as a pairwise addition of Morse He-Br interactions in the ground state [15]. Because of the mean-field approximation involved, the He-He interaction  $V$  was modeled as a Morse potential [16] including a truncated core [17],  $V(\rho) \rightarrow V(\rho) \exp[-\gamma V(\rho)]$ , where  $\gamma = 2000$  a.u. $^{-1}$  was adjusted to agree with diffusion Monte Carlo results for all sizes of boson clusters. The masses (amu) used are  $m_{\text{Br}} = 78.91830$ ,  $m_{^3\text{He}} = 3.01604$ , and  $m_{^4\text{He}} = 4.00260$ . A grid of 5000 points in the range (1.5–18.5 Å) was employed to get the radial  $g_n$  functions by a Numerov

procedure at  $n_{\text{max}} = 4$  orientations for fixed bromine bond lengths  $r = 2.20, 2.281, \text{ and } 2.35$  Å. For  $Y_{lm}$ , convergence was achieved using  $l_{\text{max}} = 8$ ,  $|m_{\text{max}}| = 3$  for fermions and  $l_{\text{max}} = 12$ ,  $|m_{\text{max}}| = 1$  for bosons. With these basis sets, the needed integrals were evaluated analytically in the angular variables and numerically in the radial ones [18].

The angular distribution  $\mathcal{D}^{(N)}(\theta)$ , common to all the pure clusters, consists of a central peak at  $\theta = \pi/2$  and additional side peaks at  $\theta \approx \pi/4$  and  $3\pi/4$ . The relative intensities of the side peaks increase with the cluster size. In the case of fermion/boson mixtures, an increase of the relative weight of the bosons leads to the increase of the peak at  $\theta = \pi/2$ , whereas an increase of the weight of the fermions results in an increase of the side peaks. As mentioned above, the distribution function  $\mathcal{D}^{(N)}(\theta)$  is used to average  $\Gamma_{fi}(\theta)$ , which itself exhibits maxima at  $\theta = 0, \pi/2, \text{ and } \pi$  [13]. For complexes of  $\text{Br}_2$  with pure fermions (18F) and mixtures with bosons (18F/6B and 18F/18B), Table I collects the values of  $\Lambda$  (unchanged for mixtures),  $E_{\Lambda,S}(r)$ , and  $\bar{L}$ . These values for pure bosons (18B) are  $\Lambda = 0$ ,  $E_{0,0} = -225.06, -222.17, -219.76$  cm $^{-1}$ , and  $\bar{L} = 8$ . It is clear that high energy degeneracy is exhibited by the fermion-containing complexes, and the degeneracy decreases as more boson atoms are added. To better understand this fact, note that the centrifugal term  $G$ , Eq. (6), together with  $E_{\Lambda,S}$ , plays a crucial role in building up the effective Hamiltonian of Eq. (5). At  $T = 2$  K, simulated vibrotational ( $\nu = 1 \leftarrow 0$ ) Raman spectra for the different complexes (18B, 18F, 18F/6B, and 18F/18B mixtures) are obtained using linear fits to  $E_{\Lambda,S}(r)$ , with spin-averaged VP width values of 0.92, 2.66, 2.7, and 2.8 ( $10^{-3}$  cm $^{-1}$ ), respectively. The spectra are computed with inclusion of all the  $J$  states up to  $J = 10$  to ensure convergence at that temperature. The  $\text{Br}_2(X)$  polarizabilities were taken from the literature [19]. In all the cases,  $Q$  lines lead to the most intense features [ $\sim 10$  times more intense than  $S(0)$  and  $\sim 100$  times more intense than  $O(2)$ ]. Except for pure bosons,  $R$  lines appear between  $S$  lines, and  $P$  lines appear between

TABLE I. Spin-dependent ground state characteristics of complexes composed of 18 fermions plus 0, 6, and 18 bosons, respectively:  $\Lambda$  values, energy levels (cm $^{-1}$ ) for  $\text{Br}_2$  bond lengths of 2.20, 2.281, and 2.35 (Å), respectively, and  $\bar{L}$  values.

$S$	$\Lambda$	$(^3\text{He})_{18}$		$(^3\text{He})_{18} + (^4\text{He})_6$		$(^3\text{He})_{18} + (^4\text{He})_{18}$	
		$E_{\Lambda,S}^{(18)}$	$\bar{L}$	$E_{\Lambda,S}^{(18/6)}$	$\bar{L}$	$E_{\Lambda,S}^{(18/18)}$	$\bar{L}$
0	8	-191.21, -188.40, -186.08	10	-247.25, -243.85, -241.06	13	-323.66, -318.70, -314.55	15
1	6	-191.74, -188.90, -186.58	9	-246.77, -244.38, -241.59	11	-325.98, -319.00, -314.74	14
2	7	-192.61, -189.84, -187.54	10	-248.33, -244.93, -242.14	12	-325.02, -319.71, -314.19	15
3	3	-192.99, -190.25, -187.98	8	-249.49, -246.06, -243.34	11	-333.14, -327.40, -322.57	14
4	0	-193.82, -191.11, -188.86	8	-249.29, -245.87, -243.05	11	-326.91, -321.29, -314.15	13
5	0	-191.43, -188.73, -186.49	8	-248.15, -244.98, -242.37	11	-324.52, -319.42, -314.97	15
6	0	-188.51, -185.80, -183.55	7	-247.81, -244.73, -242.19	12	-327.95, -323.10, -319.43	15
7	1	-183.53, -180.77, -178.50	5	-245.39, -242.34, -239.84	12	-332.00, -327.05, -320.69	15
8	2	-178.01, -175.26, -173.00	7	-243.23, -240.19, -237.69	13	-326.29, -323.36, -319.38	16
9	0	-172.07, -169.31, -167.06	7	-241.50, -238.45, -235.95	14	-327.94, -322.80, -318.52	16

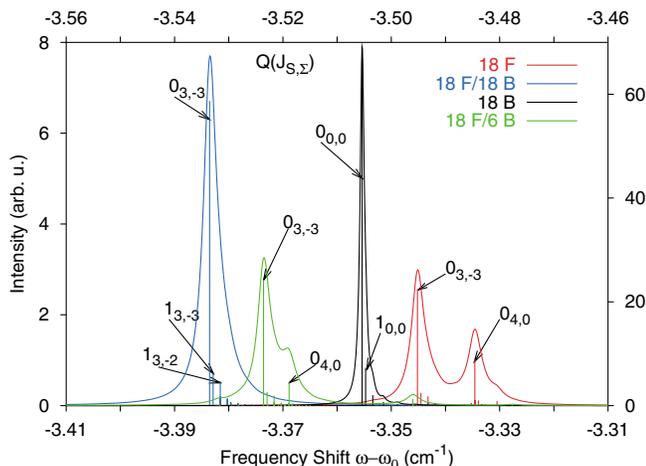


FIG. 1 (color). The  $Q$  branch region of the simulated Raman spectra corresponding to the different complexes analyzed.

$O$  lines, showing comparable intensities. Figure 1 shows the  $Q$  branch profiles for the four complexes. Assignments of the main contributing lines are indicated. Intensities for fermion complexes are shown on the left vertical axis, while those for pure bosons are indicated on the right vertical axis. For the 18F/18B complex the profile has been shifted to the right by  $0.15 \text{ cm}^{-1}$  (its corresponding frequencies appear on the top  $x$  axis). The gradual change in going from a broad profile (arising from several contributing lines) for pure fermions to the apparent single peak for pure bosons is clear from examination of the successive mixtures. Hence, the spin multiplicity emerges as the main physical feature responsible for the effect observed experimentally.

In summary, we performed quantum chemistry-type calculations for complexes of a  $\text{Br}_2$  molecule with bosonic and/or fermionic He atoms using the adiabatic approximation for the vibrations of the bromine molecule. The wave functions were then used to obtain vibrotational Raman spectral lines broadened through a modeling of the VP processes. Inspection of the most intense  $Q$  branch of the spectra computed for the cases of 18 bosonic, 18 fermionic, and mixed 18F/6B and 18F/18B He atoms leads to the following observations consistent with the features in the measured spectra [1]: (1) A single narrow peak for the case of a pure bosonic He cluster, (2) a broad structure emerging from the overlap of several peaks corresponding to different multiplicities for the case of a pure fermionic He cluster, and (3) narrowing of the spectral line shape as the percentage of the bosonic He atoms in a mixed cluster increases. It would be of interest to extend the approach described here to helium clusters doped with polar diatomic molecules, such as carbon monoxide (CO) and hydrogen fluoride (HF), for which IR spectra have been measured recently [20,21].

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