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Collision-induced Raman scattering by rare-gas atoms: The isotropic spectrum of Ne–Ne and its mean polarizability

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We report the room-temperature isotropic collision-induced light scattering spectrum of Ne–Ne over a wide interval of Raman shifts, and we compare it with the only available experimental spectrum for that system as well as with spectra calculated quantum-mechanically with the employ of advanced ab initio-computed data for the incremental mean polarizability. The spectral range previously limited to 170 cm−1 is now extended to 485 cm−1 allowing us to successfully solve the inverse-scattering problem toward an analytic model for the mean polarizability that perfectly matches our measurements. We also report the depolarization ratio of the scattering process, lingering over the usefulness of this property for more stringent checks between the various polarizability models. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4919639]

I. INTRODUCTION

The quest for thoroughly measured and calculated collision-induced scattering spectra by rare gas atoms, together with the understanding of how dipole-dipole polarizabilities associated with these spectra depend on interatomic separation, is a long-standing but still not clearly solved issue.1 Owing in part to the filled 2p subshell, neon is particularly intriguing as a system, exhibiting peculiarities that still elude understanding. To get an overview from different areas of scientific inquiry, let us cite a few from the wealth of examples. Certain spectral lines, normally expected to show up in atomic spectra of ions within the neon isoelectronic sequence, are absent from these spectra.2,3 More recently, a delay in the photoemission of the 2p electrons with respect to 2s electrons of atomic neon was measured and calculated,4 offering evidence for “small-talk” interactions between electrons. In a more chemical context, the property of neon compounds to be unstable or only marginally stable (and paradoxically enough less stable in general than their helium counterparts) was recently put forward by scientists pondering on the peculiarity of neon among the noble gases and whether it should occupy the top-right position in the periodic table.5

Neon has been for long in the forefront of many studies in atomic and molecular spectroscopy for its property to be the fourth most abundant element in the universe. Hazy atmospheres containing neon have been mentioned in the past, and they have even been proposed to decipher some unexplained properties observed in Pluto or in trans-neptunian objects.6 As regards the Raman spectrum of gaseous neon, collision-induced light scattering by this gas has provided evidence of a quantum overlap/exchange interaction term in the polarizability anisotropy of the pair that is tightly coupled to classical electrostatic interaction.7 The interference of these terms manifests itself in the form of a slope-changing spectral shape (in a logarithmic plot), a behavior never seen before experimentally in any atomic system. The position where this change of slope is produced on the frequency-axis and the way in which the spectrum falls off in the wing were shown to depend strongly on the amount of electron correlation included in the anisotropy of the atomic pair at short interatomic separations R, and can suggest a stringent criterion in measuring this effect. An extensive analysis of the anisotropic Ne–Ne spectrum and of its anisotropy β(R) has only just been published.8

But what about the isotropic spectrum of Ne–Ne? The present article is a contribution in that direction. Owing to the overall small effect of the diagonal part of the induced polarizability tensor for atomic pairs, incremental-trace light scattering is difficult to observe by atomic gases. As regards neon, in particular, only little and fragmentary information exists about the binary isotropic spectrum, with the only measurements for that spectrum being reported long time ago, by Frommhold and coworkers,9,10 in the Raman-frequency range 10 ≤ v ≤ 170 cm−1. These scientists reported a very weak intensity for that component (as compared to the intensity of the anisotropic component), a result which is consistent with the general property of rare-gas collision-induced spectra to be little polarized.

In this article, we address the issue of the isotropic spectrum of Ne–Ne, reporting absolute intensities of unprecedented accuracy within a Raman-frequency range never explored before experimentally: 100 ≤ v ≤ 485 cm−1. We show that the lineshape of that spectrum falls off purely exponentially above ~100 cm−1 and that its integrated intensity is about 30 times smaller than that of its anisotropic counterpart. Besides of being an achievement in itself, the augmented knowledge of the isotropic spectrum allowed us to derive converted

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values of even-numbered and odd-numbered spectral moments $M_6, M_1, \ldots, M_6$, an information which was instrumental in solving the inverse scattering problem for the mean polarizability $\alpha(R)$ and in assessing the quality of the solution. The analytic function that we propose below for $\alpha(R)$ reproduces consistently our observations, as well as data of the refractivity second virial coefficient $B_2$ at the temperature and wavelength of the experiment. Besides, quantum lineshapes are computed with the employ of advanced \textit{ab initio} calculation methods\cite{11,12} for $\alpha(R)$, which are critically compared with each other as well as with those of the inverse-scattering solution and with the experiment. Conclusions are drawn as to the amount of electron correlation included in the \textit{ab initio} data, especially after a close analysis of how the depolarization ratio $\eta$ depends on $\nu$, suggesting $\eta$ as a sensitive probe of correlation effects in atomic pairs.

II. THE EXPERIMENT IN BRIEF

The experiments were carried out with equipment widely recognized for its sensitivity and entirely manufactured in our laboratory.\cite{13} The detailed presentation of its components has been made elsewhere.\cite{8,13} Raman signals for at least five values of gas density ($\rho$, in amagat units) were analyzed in the frequency range $100 \leq \nu \leq 250$ cm$^{-1}$, allowing us to reliably extract from the recordings the contributions which go as $\rho^2$. This task, which permits at the end to derive the binary spectrum of neon at the zero-density limit, needs long days of continuous effort to be accomplished. Ternary and higher-order interactions were found to be negligible in the subinterval $100 \leq \nu \leq 150$ cm$^{-1}$ up to a gas density as high as 150 amagat. A systematic study, made on the basis of several experimental runs for different gas density values in the region $\nu > 150$ cm$^{-1}$, revealed insignificant contributions from impurities in the sample and no evidence from ternary interactions, at any value of $\nu$ in that spectral region, up to the highest working gas density (240 amagat); all the reported measurements beyond 300 cm$^{-1}$ were taken at 240 amagat to ensure signals that were both strong and binary. The binary signals were subsequently calibrated on an absolute scale (cm$^5$) by means of hydrogen gas (the integrated intensity of the $S_0(0)$ line due to rotational transition $J = 0 \rightarrow 2$, at 355 cm$^{-1}$, was used as a reference); the calibration procedure has been outlined in Ref. 13. Calibrated spectral components $I_\parallel(\nu)$ or $I_\perp(\nu)$ were derived, depending on whether the incident-beam polarization was perpendicular ($\perp$) or parallel ($\parallel$) to the scattering plane. The isotropic spectrum, $I_{iso}(\nu)$, was subsequently deduced from the following linear combination:

$$I_{iso}(\nu) = 1.017I_\parallel(\nu) - 1.184I_\perp(\nu).$$

By means of this expression, the ideal 0°-aperture formula\cite{14} $I_{iso}(\nu) = I_\parallel(\nu) - \frac{2}{\pi}I_\perp(\nu)$ was corrected to account for the finite aperture of the scattered beam\cite{10} (half-angle amounting to $8°$ in our experiment).

The collision-induced Raman spectra of atomic gases are well known for being nearly depolarized at small values of $\nu$, a general property translated mathematically by $\eta \approx \frac{\nu}{\nu}$. Given the definition $\eta = I_\parallel/I_\perp$, the two terms in Eq. (1) almost cancel out at small values of $\nu$, which makes the extraction of isotropic Ne–Ne intensities an unreliable operation below 100 cm$^{-1}$. Only measurements taken above 100 cm$^{-1}$ are numerically meaningful and are reported below.

Figure 1 shows the isotropic Ne–Ne spectrum as a function of $\nu$. Measurements are depicted by symbols. Quantum lineshapes, obtained with the employ of the inverse-scattering model (see below) and by the \textit{ab initio} data of Refs. 11 and 12 for $\alpha(R)$, are shown over the interval $[0 : 500]$ cm$^{-1}$. The blank in the interval $[320 : 372]$ cm$^{-1}$ is because of the occurrence of residual hydrogen around 355 cm$^{-1}$ (the $S_0(0)$ line of this gas at that frequency was used earlier as a reference for signal calibration); of course, appropriate interpolation of this portion was ensured before starting doing any calculations with this spectrum. No other experiments exist above 170 cm$^{-1}$ to allow for comparisons; satisfactory agreement was found between our data and the ones of Ref. 10 in the common interval $100 \leq \nu \leq 170$ cm$^{-1}$; we note in passing that the measurements of Ref. 9 were corrected 1 yr later in a subsequent article.\cite{16} Values of the intensity $I_{iso}$ over the interval $[100 : 485]$ cm$^{-1}$ are gathered in Table I. On the basis of the dispersion of the measured data, the error-bars for $\nu < 100$ cm$^{-1}$ turned out to be huge (the Raman signal intensities in this region being mainly controlled by the subtraction of two spectral components of almost comparable magnitude). Conversely, the dispersion of the data is shrinking quickly for $\nu > 100$ cm$^{-1}$, since the depolarization ratio of the scattering process falls off rapidly away from the resonance (attaining near-zero values for $\nu \approx 250$ cm$^{-1}$, see below). This improvement in accuracy is all the more apparent for $\nu > 230$ cm$^{-1}$ in view of the change in the detection mode (use of a CCD instead of a photomultiplier; see Ref. 8, Sec. II therein). However, this trend toward higher accuracies as...
TABLE I. Absolute-unit isotropic Raman scattering intensity ($\times 10^{-60}$ cm$^6$) by Ne–Ne as a function of Raman frequency shift (cm$^{-1}$) at 294.5 K. The total experimental error is ±60%, ±54%, ±17%, ±26%, ±22%, and ±27%, at $\nu = 125, 150, 200, 263, 270$, respectively.

<table>
<thead>
<tr>
<th>$\nu$</th>
<th>$I_{100}$</th>
<th>$\nu$</th>
<th>$I_{100}$</th>
<th>$\nu$</th>
<th>$I_{100}$</th>
</tr>
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<tbody>
<tr>
<td>100</td>
<td>443</td>
<td>280</td>
<td>16.8</td>
<td>415</td>
<td>1.73</td>
</tr>
<tr>
<td>125</td>
<td>235</td>
<td>290</td>
<td>13.9</td>
<td>420</td>
<td>1.75</td>
</tr>
<tr>
<td>150</td>
<td>185</td>
<td>300</td>
<td>13.3</td>
<td>425</td>
<td>1.47</td>
</tr>
<tr>
<td>175</td>
<td>122</td>
<td>310</td>
<td>11.2</td>
<td>430</td>
<td>1.41</td>
</tr>
<tr>
<td>200</td>
<td>74.7</td>
<td>320</td>
<td>9.42</td>
<td>435</td>
<td>1.26</td>
</tr>
<tr>
<td>220</td>
<td>48.4</td>
<td>372</td>
<td>3.45</td>
<td>440</td>
<td>1.10</td>
</tr>
<tr>
<td>240</td>
<td>49.5</td>
<td>380</td>
<td>3.40</td>
<td>445</td>
<td>1.10</td>
</tr>
<tr>
<td>250</td>
<td>44.0</td>
<td>385</td>
<td>2.90</td>
<td>450</td>
<td>0.865</td>
</tr>
<tr>
<td>260</td>
<td>36.7</td>
<td>390</td>
<td>2.72</td>
<td>460</td>
<td>0.953</td>
</tr>
<tr>
<td>265</td>
<td>37.9</td>
<td>400</td>
<td>2.30</td>
<td>470</td>
<td>1.05</td>
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<tr>
<td>270</td>
<td>23.8</td>
<td>405</td>
<td>2.04</td>
<td>475</td>
<td>0.786</td>
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<td>270</td>
<td>20.5</td>
<td>410</td>
<td>2.01</td>
<td>485</td>
<td>0.726</td>
</tr>
</tbody>
</table>

$\nu$ is increased is quickly dominated by the opposite trend, i.e., by the natural property of accuracy to deteriorate, owing to the exponential decrease in the Raman signal, which causes the error to eventually blow up to values above ±30% for $\nu > 450$ cm$^{-1}$.

III. THEORY AND NUMERICAL IMPLEMENTATION

A. Ab initio computed polarizability and quantum lineshapes

Among the existing models for the incremental polarizability of neon, the models obtained with advanced *ab initio* calculation methods, such as coupled-cluster theory with single and double excitations (CCSD), and with perturbative inclusion of triple excitations (CCSD(T)), clearly stand out from the rest, providing the literature with numerical data whose performance is expected to meet to a large extent the requirements of modern experimental tools. It is one of the purposes of this article to evaluate the degree of reliability of CCSD(T), as well as of self-consistent-field (SCF) and frequency-corrected CCSD(ω) data-sets for $\alpha(R)$, offering insight into those methods especially in relation with the amount of electron correlation included in the calculations for two closely approaching atoms.

For the calculation of spectra, the computation procedures outlined in Refs. 15 and 16 were used. Being based upon a Fox-Goodwin integrator and discrete variable representations (DVR) to ensure reliable lineshapes, these procedures have repeatedly proven themselves in practice. Any of the sets of *ab initio* data for $\alpha(R)$ used as input in these numerical procedures was expressed as a six-parameter analytic function of $R$, which was chosen to be the same for all the *ab initio* data models and which reads $P_{\text{fit}}(R) = A_6 R^6 + A_8 R^8 + A_{10} R^{10} + A_{12} R^{12} - e^{-(R-\gamma)^2}/\rho$. The choice of this function was dictated by Hättig *et al.* who have used $P_{\text{fit}}(R)$ to take the best fit to their own CCSD and CCSD(ω) series of data points. Here, we are using the same function as before, in order to curve-fit previously reported SCF, CCSD and CCSD(T) data and to ensure a smooth extrapolation up to 300 bohrs for the purpose of obtaining fully convergent matrix-elements for line-shape computations; this extrapolation for the SCF and CCSD numerical data provides, as it should, values for the coefficient $A_8$ which are globally consistent with the asymptotic leading-order dipole-induced dipole (DID) and hyperpolarizability term constants $4\alpha_0^2$ and $4\beta_0^3 + 5\gamma_0^2$, respectively. Table II gathers the values of the six fit parameters of $P_{\text{fit}}$ for the various *ab initio* models of $\alpha(R)$.

### TABLE II. Values of fit parameters of the incremental mean polarizability models tested herein.

The function reads $P_{\text{fit}}(R) = A_6 R^6 + A_8 R^8 + A_{10} R^{10} + A_{12} R^{12} - \exp{-(R-\gamma)^2}/\rho$ as reported by Hättig *et al.* for the purpose of fitting their own *ab initio* data. The units of $\sigma$, $\rho$, $A_6$, $A_8$, $A_{10}$ and $A_{12}$ are $\sigma_0$, $\rho_0$, $A_6^*$, $A_8^*$, $A_{10}^*$ and $10^3 A_{12}^*$, respectively.

<table>
<thead>
<tr>
<th>$\sigma$</th>
<th>$\rho$</th>
<th>$A_6$</th>
<th>$A_8$</th>
<th>$A_{10}$</th>
<th>$A_{12}$</th>
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<tr>
<td>SCF$^a$</td>
<td>0.533 280</td>
<td>5.46065</td>
<td>70.4613</td>
<td>-3417.10</td>
<td>4.61706</td>
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<tr>
<td>CCSD$^a$</td>
<td>0.923 847</td>
<td>4.99223</td>
<td>227.130</td>
<td>-5225.26</td>
<td>5.16028</td>
</tr>
<tr>
<td>CCSD(T)$^a$</td>
<td>1.008 61</td>
<td>4.90318</td>
<td>292.308</td>
<td>-5610.95</td>
<td>4.63215</td>
</tr>
<tr>
<td>CCSD$^b$</td>
<td>0.783 255</td>
<td>5.34016</td>
<td>297.685</td>
<td>-6905.68</td>
<td>5.98060</td>
</tr>
</tbody>
</table>

$^a$Reference 11.

$^b$Reference 11.
and classical-like spectra: $I_{iso}^c(\nu) = 1-e^{-\frac{h\nu}{k_B T}}I_{iso}(\nu)$ (superscript “c” stands for classical-like; $h$ and $k_B$ are the Planck and Boltzmann constants, respectively; $T$ is absolute temperature); this point is fully outlined in Ref. 8 (Sec. III B and Figure 1, therein).

In the present work, the incremental mean polarizability was given the following 4-parameter form:

$$
\alpha(R) = \alpha_{DID}(R) + \frac{5yC_0}{9\alpha_0 R^6} + \frac{20\gamma C_q}{R^8} + \frac{X_1}{R^{10}} + \frac{X_3}{R^{12}} - X_4 e^{-X_5 R^2},
$$

with $X_1$, $X_2$, $X_3$, and $X_4$ as the parameters we seek to optimize (the former two being defined as positive). A quadratic decaying exponential was used in Eq. (2) to mimic the overlap/exchange interaction; terms to orders $R^{-10}$ and $R^{-12}$ were added to enhance the flexibility of the functional; $\alpha_{DID}(R)$, $\alpha_0$, $\gamma$, $C_q$, and $C_0$ designate all-orders DID$^{17}$ and atomic polarizability at the frequency of the experiment, second hyperpolarizability, quadrupole polarizability, and first long-range dispersion coefficient of the Ne···Ne interaction potential, respectively; the values of these parameters have been given in Ref. 8; switching from the dynamic (2.693 $a_0^3$) to the static value (2.669 $a_0^3$) of $\alpha_0$ in the expressions for $\alpha_{DID}(R)$ and $\alpha(R)$ did not show noteworthy effects on the mean polarizability $\alpha(R)$, and only very slightly affected the spectrum.

There are four parameters to be optimized, hence an equal number of conditions need to be introduced as criteria for convergence. The three low-order classical sum-rule expressions, $M_0$, $M_2$, and $M_4$, and the equation for the refractivity second virial coefficient $B_8$ were employed for the purpose.$^{23,24}$ As we show below via a posteriori comparison, the close agreement between the values of spectral moments $M_0$, $M_2$, and $M_4$ and the values derived from the experiment with those derived from the quantum lineshape due to the optimized model of Eq. (2) lends full credence to the quality of the proposed model for $\alpha$.

The expressions for the zeroth-, second-, and fourth-order classical sum rules in isotropic scattering read$^{25}$

$$
M_0 = 4\pi \int_0^{\infty} \alpha^2 g(R) R^2 dR,
$$

$$
M_2 = \frac{4\pi k_B T}{\mu} \int_0^{\infty} \alpha^2 g(R) R^2 dR,
$$

$$
M_4 = 4\pi \left( \frac{k_B T}{\mu} \right)^2 \int_0^{\infty} \left[ 3\alpha^\prime \alpha^\prime \prime + \left( \frac{8}{R^3} - \frac{4U^\prime}{R} + U^2 \right) \alpha \right] g(R) R^2 dR,
$$

$$
M_n = \left( \frac{A}{2\pi} \right)^n (2\pi e)^n \int_{-\infty}^{+\infty} I_{iso}(\nu) \nu^n d\nu,
$$

where $g(R) = e^{-U} = e^{-\frac{V(R)}{k_B T}}$ is the classical radial distribution function, with $V(R)$ as the interaction potential of Ne···Ne; the Aziz-Slaman HFD-B (Hartree-Fock-Dispersion-B) model was used for the potential,$^{26}$ both for computations of line-shapes and for the inversion procedure; $\mu$ is the reduced mass; $\lambda(=514.5 \text{ nm})$ is the laser wavelength, $\alpha'$ and $\alpha''$ designate first and second derivatives with respect to $\nu$.

In Figures 2 and 3, the classical quantities $\nu^4 I_{iso}^c(\nu)$ are shown for $n = 0$ and $n = 2$ and 4, respectively. The observation that the curves for $n = 0$ and 2 have reached near-zero levels at $\nu = 485 \text{ cm}^{-1}$ shows that the values of the spectrally calculated moments $M_0$ and $M_2$ have converged. As for $M_4$, a missing 4% in the area of $\nu^4 I_{iso}^c(\nu)$ below the $n = 4$ curve (Fig. 3) had to be completed in order for the convergence of $M_4$ to be accomplished. In order to compensate for the lack of experimental data below 100 cm$^{-1}$ in the isotropic spectrum, the quantum lineshape generated by the CCSD($\omega$) model of Ref. 11 was used (this spectrum portion is shown in dashed in

**FIG. 2.** Symmetrized (“classical”) spectrum $I_{iso}^c(\nu)$ (cm$^4$), shown at both spectral sides, as a function of $\nu$ (cm$^{-1}$) (solid line curve). Our measurements are shown for comparison (symbols). To override the lack of experimental data below 100 cm$^{-1}$, the spectrum was extrapolated in the interval [0:100] cm$^{-1}$ by using a portion of the CCSD($\omega$) profile (long-dashed line curve). The asymmetric spectrum (short-dashed line curve) is the actual spectrum (values at $\nu < 0$ were obtained from the $\nu > 0$ ones by applying the principle of detailed balance).

**FIG. 3.** Classical quantities $I_{iso}^c(\nu)\nu^n$ (cm$^{-1}$) as a function of $\nu$ (cm$^{-1}$) for $n = 2(\times 10^5)$ and $n = 4$. 

The corresponding spectral moments, associated with the classical spectrum, are
Figs. 2 and 3). The choice of this specific ab initio data-set to model the missing portion of the spectrum was motivated by criteria such as (i) the high level of optimization employed for these data, (ii) their excellent spectral response (on the basis of a comparison with our measurements, Fig. 1), and (iii) the use, for their calculation, of an extended orbital basis set (the adequacy of augmented, well-balanced Dunning’s correlation-consistent polarized valence orbital bases has already been shown in the description of rare gas pair-polarizability tensors^8,18,27). The following values were thus obtained and used to feed the inversion procedure:

\[ M_0 = 7.85 \times 10^{-4} \text{Å}^9, M_2 = 1.94 \times 10^{-1} \text{Å}^9 \text{ps}^{-2}, M_4 = 2.23 \times 10^{-2} \text{Å}^9 \text{ps}^{-4}. \]

According to the CCSD(ω) data of Refs. 11, 28, and 29 for the refractivity second virial coefficient at the temperature and the wavelength of the experiment, the value \( B_R = -9.91 \times 10^{-2} \text{cm}^6 \text{mol}^{-2} \) was taken for the fourth input. It is reassuring that this value is consistent with the state of the art of experimental refractivity data for neon (Refs. 30–35); these data are shown listed in Table III.

The refractivity second virial coefficient at frequency \( \omega \) was calculated from the expression,

\[ B_R(\omega) = B_e + \omega^2 B_R^{(2)} + \cdots, \]

with \( B_e \) as the dielectric second virial coefficient,

\[ B_e = \frac{8\pi^2 N_A^2}{3} \int_0^\infty \alpha(R)g(R)R^2dR, \]

and \( B_R^{(2)} \) the dispersion contribution,\(^1\)

\[ B_R^{(2)} = \frac{8\pi^2 N_A^2}{3} \int_0^\infty \Delta \alpha(-4)g(R)R^2dR. \]

\( N_A \) is the Avogadro constant; \( \alpha(R) \) is the static mean incremental polarizability; \( \Delta \alpha(-4) \) is the associated fourth-order Cauchy moment.

**TABLE III.** Values for \( B_R(\omega) \) and \( B_e \) from refractivity (R) and dielectric-constant (\( \epsilon \)) experiments, shown for various wavelengths at near room temperature in a reverse chronological order. Values for the theoretical dispersion, \( B_R^{(2)}(T) \), calculated from Eq. (9) by using the CCSD(\( \omega \)) value of \( \Delta \alpha(-4) \) (Ref. 11) are also given. \( T, A, B_R, B_e, \) and \( B_R^{(2)} \) are expressed in units of K, nm, cm\(^6\) mol\(^{-2}\), cm\(^6\) mol\(^{-2}\), and cm\(^6\) mol\(^{-2}\) (a.u.)\(^2\), respectively; \( \omega = 2\pi c/\lambda \) is in atomic units (1 a.u. of \( \omega = 4.1344 \times 10^{16} \text{ s}^{-1} \).

<table>
<thead>
<tr>
<th>Method</th>
<th>( T )</th>
<th>( \lambda )</th>
<th>( B_R(\omega) )</th>
<th>( B_e )</th>
<th>( B_R^{(2)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \epsilon )</td>
<td>242.95</td>
<td>514.5</td>
<td>-0.104(21)^2</td>
<td>-0.10(2)</td>
<td>-0.5523</td>
</tr>
<tr>
<td>( \epsilon )</td>
<td>323.15</td>
<td>514.5</td>
<td>-0.125(63)^2</td>
<td>-0.12(6)</td>
<td>-0.5996</td>
</tr>
<tr>
<td>( \epsilon )</td>
<td>298.2</td>
<td>457.9</td>
<td>-0.11(22)</td>
<td>-0.11(2)</td>
<td>-0.5996</td>
</tr>
<tr>
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<td>632.8</td>
<td>-0.14(14)</td>
<td>-0.14(14)</td>
<td>-0.5996</td>
</tr>
<tr>
<td>( \epsilon )</td>
<td>303.15</td>
<td>632.8</td>
<td>-0.11(2)</td>
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<td>-0.5996</td>
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<tr>
<td>( \epsilon )</td>
<td>323.15</td>
<td>514.5</td>
<td>-0.225(20)^2</td>
<td>-0.22(2)</td>
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<td>-0.06(9)</td>
<td>-0.06(9)</td>
<td>-0.5996</td>
</tr>
</tbody>
</table>

Technically, a Newton-Raphson matrix-equation solver was implemented whose recursive formula reads

\[ X_{i+1} = X_i - D^{-1}f(X_i). \]

For a detailed description of this solver the reader is invited to refer to a previous publication;\(^18\) here, \( D \) is the Jacobian matrix

\[ D(X) = \begin{pmatrix} \partial M_0 / \partial X_1 & \partial M_0 / \partial X_2 & \cdots & \partial M_0 / \partial X_4 \\ \partial X_1 & \partial X_2 & \cdots & \partial X_4 \\ \partial M_2 / \partial X_1 & \partial M_2 / \partial X_2 & \cdots & \partial M_2 / \partial X_4 \\ \partial X_1 & \partial X_2 & \cdots & \partial X_4 \\ \partial M_4 / \partial X_1 & \partial M_4 / \partial X_2 & \cdots & \partial M_4 / \partial X_4 \\ \partial X_1 & \partial X_2 & \cdots & \partial X_4 \\ \partial M_R / \partial X_1 & \partial M_R / \partial X_2 & \cdots & \partial M_R / \partial X_4 \\ \partial X_1 & \partial X_2 & \cdots & \partial X_4 \end{pmatrix}. \]

its elements read

\[ D_{ab} = 4\pi \int_0^{\infty} f_{ab}(X_g)(R)R^2dR; \]

\( X \) and \( F(X) \) are abbreviations for vectors \((X_1, X_2, X_3, X_4) \) and \((\Delta M_0, \Delta M_2, \Delta M_4, \Delta M_R) \), respectively. The latter is a vector whose components are increments defined at each step of the procedure by the difference between the running and the input moment and refractivity-coefficient values; it corresponds to the vector that we seek to vanish upon completion of the program. The formal expressions for \( f_{ab} \) along with expressions for the derivatives of \( \alpha(R) \) with respect to \( R \) and \( X_a \) are given as the supplementary material.\(^\text{36}\)

Well-defined plateaus of stability were found, yielding the following values for the optimized parameters: \( X_1 = 2.21435 \times 10^3 \text{a}_0^2 \), \( X_2 = 1.48776 \times 10^{-1} \text{a}_0^2 \), \( X_3 = 2.13601 \times 10^3 \text{a}_0^2 \), and \( X_4 = -3.43139 \times 10^6 \text{a}_0^2 \).

**IV. COMPARISONS AND DISCUSSION**

To allow for a critical comparison between models, Figure 4 illustrates the inverse-scattering solution of Eq. (2)

![FIG. 4. The mean polarizability of Ne-Ne, \( \alpha \) (in a.u.), as a function of \( R \) (bohr). The inverse-scattering model of Eq. (2) is compared with the CCSD(T), CCSD and SCF data of Ref. 12 and the CCSD and CCSD(\( \omega \)) data of Ref. 11. Distances \( <4 \) bohrs are not detectable experimentally at 294.5 K. In the inset, the range [6.5:8.5] bohrs is shown enhanced to highlight the effect of electron correlation on the bump.](image-url)
together with the \textit{ab initio} computed data for the incremental mean polarizability. A substantial drop in the concave part of the curves along with a slight rise in their top as one moves to higher optimization levels in the computation of $\alpha(R)$ is observed in the intervals $[4 : 6.5]$ and $[6.5 : 8.5]$ bohrs (see inset), respectively, which suggests a cause-and-effect relationship between these trends and the amount of electron correlation effectively included in the calculation at short $R$. Just as one expects from an \textit{ab initio} calculation, at close separations, SCF$^{12}$ is shown to contain the smallest amount of electron correlation whereas CCSD(T)$^{12}$ is the largest. When focusing on CCSD, the [7s5p4d1f] orbital basis set of Ref. 12 seems to be slightly disfavored against the d-aug-cc-pVQZ-33211 basis of Ref. 11, and the effect of dynamic corrections [CCSD($\omega$)] to the static version of CCSD$^{11}$ to be small; both CCSD and CCSD($\omega$) curves are situated in between SCF and CCSD(T). Of all the data sets, the inverse-scattering solution is shown to perform the best. This is all the more interesting, as incremental mean polarizabilities are properties of higher order than are anisotropies (in the sense of their $1/R$-power series expansion), and as such \textit{ab initio} calculations for these properties are much more difficult to converge. Let us finally glance back to Fig. 1 for a fuller comparison between the various isoelectronic series, shown in Fig. 4 in relation with their spectra. A more critical analysis, based upon comparisons between the various lineshapes, shown in Fig. 1 (curves), and the experimental data (symbols) can thus be made, which leads to conclusions that are consistent with those drawn above from the analysis of Fig. 4.

In Figure 5, the depolarization ratio $\eta$ is shown plotted as a function of $\nu$; numerical data are gathered in Table IV. The property of Ne–Ne scattering to be a totally depolarized process close to resonance and to become gradually more polarized as $\nu$ is increased is basically an expected behavior: binary scattering for high values of $\nu$ is nothing but the spectral manifestation of two closely spaced units (in the language of Fourier transformations) and, therefore, of a supramolecular entity behaving more isotropically than if its units were far apart. Interestingly, however, a marked rise, faithfully reproduced by our model (while not predicted by any of the existing \textit{ab initio} polarizability calculations) is observed beyond 250 cm$^{-1}$. By comparison, differences that are less marked than the ones observed in $\eta$ are noted on the lineshapes of $I_{iso}$ and $I_{f}$, shown plotted in Fig. 1 and Ref. 8 (Fig. 5, therein), respectively. This observation suggests that depolarization ratios can be used as stringent tests of polarizability models (owing to their property of being both sensitive to slight variations and able to assess, simultaneously, the quality of $\alpha$ and $\beta$) and further validates the claim that inverse-scattering models for $\alpha$ and $\beta$ contain information at close separations that may be unaccounted for in the \textit{ab initio} calculations. It is worth mentioning that a qualitatively similar pattern as that of Fig. 5 was found for the depolarization ratio of Ne–Ar (see Fig. 4 in Ref. 27).

Table V gathers values for even-numbered and odd-numbered spectral moments up to $M_6$. These values were obtained by carefully integrating the measured and the quantum lineshapes. The close agreement that we observe in comparing the entries of this table for the most reliable

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|}
\hline
$\nu$ & 4.0 & 7.0 & 10.0 & 12.5 & 15.0 & 17.5 & 20.0 & 22.5 & 25.0 & 50.0 & 75.0 & 100.0 & 125.0 & 150.0 & 175.0 \\
\hline
$\eta$ & 0.869 & 0.879 & 0.896 & 0.889 & 0.870 & 0.917 & 0.871 & 0.893 & 0.882 & 0.866 & 0.809 & 0.608 & 0.554 & 0.294 & 0.166 \\
\hline
$\nu$ & 200.0 & 220.0 & 225.0 & 230.0 & 240.0 & 250.0 & 255.0 & 263.0 & 270.0 & 280.0 & 290.0 & 300.0 & 310.0 & 320.0 & 372.0 \\
\hline
$\eta$ & 0.133 & 0.103 & 0.092 & 0.077 & 0.069 & 0.072 & 0.067 & 0.064 & 0.069 & 0.076 & 0.079 & 0.064 & 0.068 & 0.070 & 0.131 \\
\hline
\end{tabular}
\caption{The depolarization ratio of Ne–Ne as a function of Raman shift $\nu$ (cm$^{-1}$).}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|}
\hline
$M_0$ & $M_1$ & $M_2$ & $M_3$ & $M_4$ & $M_5$ & $M_6$ \\
\hline
Expt. & 8.36 & 2.59 & 2.12 & 2.95 & 2.67 & 9.23 & 9.25 \\
Inversion & 8.29 & 2.62 & 2.14 & 2.87 & 2.61 & 9.19 & 9.30 \\
$^a$CCSD(T) & 8.54 & 3.00 & 2.45 & 3.43 & 3.11 & 9.86 & 9.17 \\
$^a$CCSD & 8.42 & 2.81 & 2.30 & 3.19 & 2.90 & 9.20 & 8.57 \\
$^{b}$CCSD & 7.80 & 2.60 & 2.13 & 2.92 & 2.65 & 8.37 & 7.79 \\
$^{b}$CCSD($\omega$) & 8.45 & 2.68 & 2.19 & 3.10 & 2.73 & 8.86 & 8.50 \\
SCF & 6.36 & 1.88 & 1.53 & 2.09 & 1.89 & 6.04 & 5.64 \\
\hline
\end{tabular}
\caption{Spectral moments calculated from measured (expt, this work) and quantum lineshapes. The quantum line shapes were calculated with the employ of either the inversion model (inversion, this work) or the \textit{ab initio} data of Maroulis and Hättig \textit{et al.} for the incremental mean polarizability. Values of $M_0$, $M_1$, $M_2$, $M_3$, $M_4$, $M_5$, and $M_6$, are expressed in units of $10^{-3}$ $\text{Å}^3$, $10^6$ $\text{Å}^2$ s$^{-1}$, $10^{13}$ $\text{Å}^3$ s$^{-2}$, $10^{16}$ $\text{Å}^4$ s$^{-3}$, $10^{19}$ $\text{Å}^5$ s$^{-4}$, $10^{22}$ $\text{Å}^6$ s$^{-5}$, and $10^{27}$ $\text{Å}^7$ s$^{-6}$, respectively.}
\end{table}
TABLE VI. Theoretical values for $\beta_C$ at 294.5 K, calculated from the various data for $\alpha(R)$ with the employ of the potential of Ref. 26 and of Eq. (8).

<table>
<thead>
<tr>
<th>Inversion</th>
<th>CCSD(T)</th>
<th>CCSD($\omega$)</th>
<th>CCSD</th>
<th>SCF</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-0.0991^a$</td>
<td>$-0.0929^b$</td>
<td>$-0.1126^b$</td>
<td>$-0.1371^b$</td>
<td>$-0.0991^c$</td>
</tr>
</tbody>
</table>

$^a$This work.
$^b$Reference 12.
$^c$Reference 11.

Theoretical models and the experiment is the best and most convincing way to prove the validity of the methodology employed in this article.

Table VI gathers theoretical values for the second dielectric virial coefficient, $\beta_C$, calculated with the potential of Ref. 26 for the various data sets of $\alpha$, at 294.5 K. Interestingly, all the post-Hartree-Fock data of this table show agreement with the most recently measured values of $\beta_C$ (Ref. 30) within the experimental error (Table III). The inversion (this work) goes by construction to the CCSD($\omega$) value. The striking agreement between the experimentally measured values of $\beta_C$ (Ref. 30, Table III) and the value obtained with the employ of the CCSD data of Ref. 12 deserves to be emphasized.

V. SYNOPSIS

This work comes as a continuation of our recent article on the (Ne)$_2$ anisotropic spectrum and anisotropy, focusing in particular on the advantageous use of modern experimental tools, developments in theory and the assistance of advanced ab initio calculation methods in the understanding of collision-induced processes by small atomic clusters. We measured the room-temperature isotropic collision-induced Raman scattering spectrum of neon, for different values of gas density, and we derived from the measurements the Ne–Ne spectrum at the zero density limit. The reported spectrum covers a frequency range of an unprecedented extent which allowed us to obtain converged values for even-numbered and odd-numbered spectral moments up to $M_6$. We offered evidence that the higher the level of optimization in an ab initio calculation, the steeper is the $R$-dependence of the incremental mean polarizability, $\alpha(R)$, at close separations, and found that the spectral response of the ab initio calculations for $\alpha$ was gradually improving from below with increasing level of optimization. We used our previously developed approach to solve the inverse-scattering problem, and we obtained a model for $\alpha$ which identically matches the experimental data over an intensity range almost four orders of magnitude wide. Finally, we used the depolarization ratio as a better device to size up the quality of $\alpha$ and showed that even the most reliably computed data for the (Ne)$_2$ polarizability fail to monitor the variations of $\eta$ at the very high frequencies.


2120 This statement is corroborated by Table 5.3, in Ref. 19, in which various procedures have been checked and compared with the quantum profile of He–Ar at 295 K. It is obvious from that table that P2 only slightly differs from the quantum profile, underestimating by about 1.5% the intensities at the low frequencies and overestimating it by about 5% at 400 cm$^{-1}$.

22Strictly, among the several existing corrections to a classical spectrum, only the Eigenstaff correction can generate the exact quantum-mechanical lineshape [see, for instance, A. Borysow and L. Frommhold, “Collision-induced light scattering: A bibliography,” in Advances in Chemical Physics, edited by I. Prigogine and S. A. Rice (John Wiley and Sons, New York, 1989), Vol. LXXV, p. 454]. However, the implementation of this correction is lengthy and tedious since it requires to Fourier-transform the modified auto-correlation function $C(r^2 + (k/\lambda)^2)$.

23For more on why it is internally consistent to use classical sum rules in the inverse scattering procedure insofar as the harmonic symmetrization procedure is used to symmetrize the measured profile, the reader is invited to refer to Ref. 8.

24The very good response of the harmonic procedure has also been underlined elsewhere; see, for instance, a study of the quantum dynamics in simple quantum-mechanical fluids of light atoms like neon at low temperature, C. P. Lawrence, A. Nakayama, N. Makri, and J. L. Skinner, J. Chem. Phys. 120, 6621 (2004).


36See supplementary material at http://dx.doi.org/10.1063/1.4919639 for the expressions of $f_{ab}(X)$ (Part I) and of the derivatives of $\alpha(R)$ with respect to $R$ and $X_\alpha$ (Part II).