Anisotropic collision-induced Raman scattering by Ne-Ne: Evidence for a nonsmooth spectral wing

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We report the anisotropic collision-induced scattering (CIS) spectrum of two neon atoms at room temperature. The covered spectral range hitherto restricted to 170 cm^{-1} is here tripled. Both our measurements and quantum-mechanical calculations obtained on the basis of large-scale *ab initio* anisotropy representations reveal a well-defined saddle-shaped wing. This peculiar structure is experimental evidence of a binary CIS line shape with an aspect other than a smooth wing in a logarithmic plot. Equally interesting is the fact that this feature has been predicted (though only qualitatively) by the simple semiempirical model long ago reported by Meinander, Tabisz, and Zoppi [J. Chem. Phys. **84**, 3005 (1986)], but no emphasis had at that time been placed on the aspect of the wing of the model spectrum probably due to the lack of high-frequency experimental data.

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Systems can have properties not directly traceable to system's components but rather to how those components interact. Such a collective view, according to which wholes produce unique combined effects, can be summarized by the statement "the whole is greater than the sum of its parts." Collision-induced Raman scattering (CIS) is a long known phenomenon dating back to the late sixties [1]. A great deal of work has been done since then and a number of topical reviews now exist to allow the reader to have an overview of the current situation [2]. The driving mechanism of the process is the interactions between gas particles, so CIS is indeed a collective phenomenon. These interactions can be sources of light scattering through a polarizability in excess of those of the gas constituent units. This induced polarizability is no longer property of the gas particles but depends on the separation between them and on their orientation. CIS can be an effective probe of induced polarizabilities. It occurs by shining laser light onto a gas of nonreactive atoms or molecules in thermal collisions. Light is then scattered thereby at a frequency that may differ from the laser frequency. Its intensity can be measured and calculated as an appropriate scattering intensity, which turns out to depend strongly on the frequency of the scattered radiation, as well as on gas temperature and density and on the laser wavelength.

Owing to the nonadditive character of the interactions, it is no longer possible to assign CIS intensities to individual gas particles. Rather, it is essential to organize the gas into parts of different levels of complexity going beyond the level of its elementary units. Ordering the particles of a gas into "clusters" of two, three, etc. is an abstract yet very helpful assignment, which stems from the need to establish some hierarchy in the role of each of its infinitely many interacting subsystems. Each of those clusters, made up of freely moving loosely interacting atoms or molecules, is only transient. It takes existence and effect solely when some of the cluster's randomly moving particles come close to each other, an event referred to as a "collision." The closer the approach, the stronger the interactions are between overlapping electron clouds. Straight after the event has ended and those atoms or molecules have moved far enough apart, the concept of cluster loses its intuitive meaning. Owing to the combinatorial nature of light scattering, clusters of n particles scatter like $\mathcal{N}!/[n!(\mathcal{N}-n)!]\approx\mathcal{N}^n/n!$, the unordered collection of n individuals taken from a pool of $\mathcal{N}$. Validity of this approximation is obvious, given that, for 1 mole of gas, $\mathcal{N}$ equals the Avogadro's number. Scattering intensities by clusters of n particles should thus scale with gas density ρ precisely as $\rho^n/n!$, which suggests a powerful and unambiguous means for systematization of a study and for interpretation of CIS spectra.

CIS spectra have thoroughly been investigated over the last 40 years. Among the long list of contributions, Refs. [1–7] are pioneer studies in the area. Binary spectra by atomic gases, in particular, are principal manifestations of the polarizability anisotropy of an atomic pair. Anisotropy β is a function that strongly depends on interatomic separation r and which appears as a result of the broken spherical symmetry of the free atom. Until the beginning of the decade, it was tacitly admitted that binary CIS spectra share three aspects in common: the extremely rapid decrease in the intensity as frequency of scattered light moves far from resonance; a relatively high depolarization ratio of scattered radiation; a smooth wing in a logarithmic plot. However, while the first of those aspects applies without exception, there is now evidence that the two others are not universal characteristics. Thus, scattering by the lightest atomic pair, helium, gives rise, some study has shown [8], to a fully polarized spectrum in the far wing, even though typical gas spectra are indeed nearly depolarized. Equally striking is the observation reported here of an unprecedented saddle-shaped wing in Ne-Ne. This structure provides evidence for existence of nonsmooth wings in binary CIS.

The need for innovative experiments with neon and for reliable modeling of its polarizability is all the more apparent

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today given the vital role this gas is believed to play in hazy atmospheres of trans-Neptunian objects. Such a need fully justifies increasingly elaborate calculations to describe its polarizability at close separations. Despite the substantial progress accomplished in the area of CIS, the last word on the topic is yet to come. This Brief Report is a contribution in that direction. It deals with room-temperature neon gas and with the way in which light is intercepted and scattered by a pair of interacting atoms. We show below that neon scatters in a very special way, which makes this pair one of the most challenging systems among rare gas structures. Short-range effects in the Ne-Ne shape clearly mark their appearance through a well-defined structure, which was seen by our experiment. This feature, corroborated here by large-scale *ab initio* calculations, provides evidence for the existence of rototranslational CIS spectra with line shapes other than a smooth wing in a logarithmic plot.

The experiment was carried out with the setup we have developed and constantly been improving over the last ten years to achieve higher and higher sensitivity. This technology and know-how for signal detection and treatment made it possible to record the deep interior of the neon CIS spectrum. The spectrum was recorded, and is hereafter presented, over the extended frequency range $[5:450]$ cm^{-1}, which is to be compared to the ranges $[6:80]$ cm^{-1} and $[10:170]$ cm^{-1} formerly covered by the experiments of Bérard and Lallemand [9] and of Frommhold and Proffitt [6,10], respectively. Its slope reveals a pronounced break in its wing at a frequency 250 cm^{-1} away from the laser. For other pure atomic gases previously studied by our group, such as argon and helium, no similar behavior has been observed even though equally broad spectral domains have been explored. We show hereafter that this feature is predicted by the *ab initio*-obtained most sophisticated representations of neon anisotropy [11,12]. These models exhibit a common general trend and feature, in particular, a local maximum at $r \approx 4.5$ bohr. A systematic analysis showed that this unusual pattern in the anisotropy correlates directly with the saddle-shaped wing of the spectrum, a situation encountered when two interacting neon atoms severely interpenetrate into the interior of each other's van der Waals radius.

The experimental setup and general experimental procedure have been described elsewhere [13]; here, only some elements specific to the present study are given. A specially designed high-pressure four-window gas cell was used. Highly purified gas, with residual impurities less than 1 ppm, was injected to ensure negligible parasitic signals caused by any Raman-active residues possibly present in the cell. The $\lambda_L = 514.5$ nm green line of a 2 W ion-argon laser was chosen to excite the gas. Gas density ρ was deduced from the measured pressure P at temperature $T = 294.5$ K, using the virial equation of state, known to be the most interesting and versatile of the equations of state for gases. Light scattered at right angle with respect to the incident beam was spectrally dispersed through a double monochromator supplied with two holographic gratings. The light signal was detected upon exiting the monochromator by means of either of the following two devices. A -20 °C-cooled bialkali photomultiplier, combined with an amplifier discriminator and a photon counter, was used below 250 cm^{-1}. Beyond 230 cm^{-1}, the extremely weak signal had to be mapped onto the matrix of a liquid-nitrogen-cooled charge-coupled device (CCD) associated with a Super-Notch holographic filter. A 20 cm^{-1} overlapping range, where both detectors were operational, was established in order to check detector-specific data processing and to ensure zero mismatch and consistency between the two devices. Spectral resolution of the spectrometer was gradually increased from 1 to 10 cm^{-1} as frequency was increased from 5 to 250 cm^{-1}. Beyond that limit, detection switched to the CCD and resolution of the spectrograph was kept fixed at 1.2 cm^{-1}. The anisotropy component to the CIS signal, $S(\nu)$, was measured for an incident beam polarized parallel to the direction of observation. For each value of ν within the range $[5:250]$ cm^{-1}, at least five gas densities were analyzed. The density-independent binary intensity, $I(\nu)$, was carefully derived from the slope of the linear part of $S(\nu)/\rho$, that is, over density ranges in which ternary collisions, scaling cubically with density, had not yet manifest themselves. Figure 1 illustrates S/ρ (arbitrary units) as a function of ρ (amagat). Upper density bounds were fixed at 100, 150, and 240 amagat over the frequency ranges [5:25], [25:150], and $[150:250]$ cm^{-1}, respectively, so that optimal retrieval of the binary spectrum is ensured. Beyond 300 cm^{-1}, careful density analysis showed that allowed Raman spectra by Raman-active impurities had insignificant contribution to the recorded signal. The same was true with ternary interactions as long as $\rho \leq 250$ amagat. Scattering intensities were calibrated on an absolute scale (cm^6) by using as reference the integrated intensity of the $S_0(0)$ rotational line of H_2.

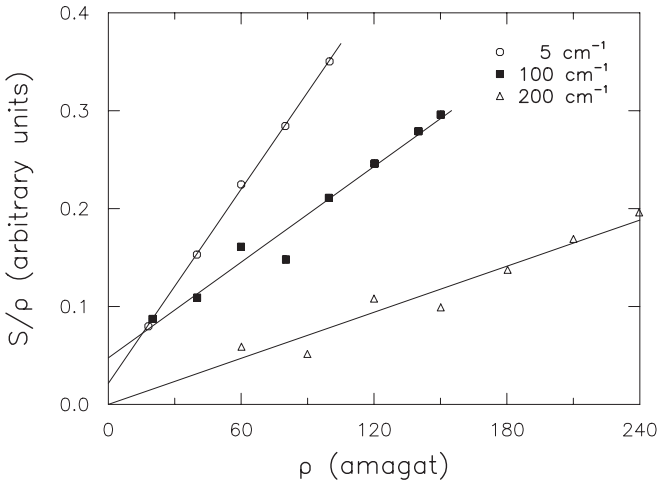

FIG. 1. S/ρ (arbitrary units) as a function of ρ (amagat) for values of ν that are representative of the low, intermediate, and high frequency parts of the spectrum. The perfect linearity of the curves is evidence for interactions that are strictly binary.

Various models of β, obtained from modern quantum-chemistry calculations for neon, were checked. CCSD(T) (coupled cluster with single, double, and partially triple excitations) calculations by Maroulis [11], properly including all single and double excitations plus perturbative connected triple excitations, offer the most reliable *ab initio* representation to date. Two other series of data, obtained at the CCSD level but using different sizes of basis sets, were also

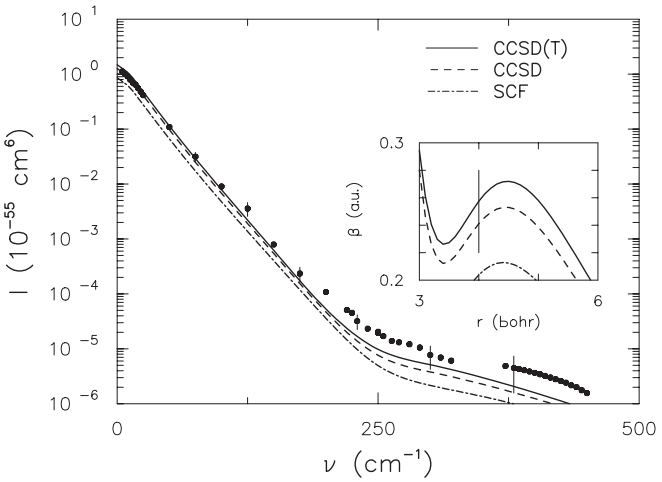

FIG. 2. Absolute anisotropic CIS spectrum of a pair of neon atoms I (cm^6) as a function of ν (cm^{-1}). Our measurements (•) are compared with quantum-mechanical spectra (curves) calculated from various *ab initio* β models. The inset illustrates the models of β (a.u.), used for the calculation of the spectra, within the range [3:6] bohr where overlap effects are particularly pronounced. In the two illustrations, same types of curves are used for clarity.

checked [11,12]. Finally, self-consistent-field (SCF) data [11] were also considered to allow the reader to better compare and contrast the methods, even though SCF calculations are far less sophisticated than the ones mentioned above. For the reliable calculation of spectra, the most rigorous theoretical framework was used, that is, quantum mechanics. To convert coordinate-dependent polarizability to frequency-dependent CIS intensity, properly weighted energy-integrated squared matrix elements were superposed over all possible values of the rotational quantum number according to formulas detailed in references [14]. The anisotropic CIS intensity is then expressed as

$$I(\nu) = \frac{2}{15}\frac{h^3 V}{Z_T} k_0 k_s^3 \langle g_J |\langle \psi_{J',E'}|\beta|\psi_{J,E}\rangle|^2\rangle, \qquad (1)$$

where ν denotes frequency shift, Z_T is the partition function at temperature T, k_0 and k_s are the wave-vector moduli for the incident and scattered electromagnetic fields, respectively, and h^3V is the phase-space normalization volume (with V the physical volume of the sample and h the Planck's constant); $\psi_{J,E}$ and $\psi_{J',E'}$ are the energy-normalized vibrational wave functions of the initial (E,J) and final (E',J') states of the pair, respectively, where E and E' denote energy, and J and J' denote rotational quantum numbers. External brackets $\langle\cdots\rangle$ denote statistical averaging over energy and angular momentum for the quasimolecule. Quantity g_J stands for nuclear statistical weight, taking values that depend on the parity of the rotational quantum number J.

Figure 2 illustrates the absolute anisotropic Raman scattering spectrum as a function of frequency. Measurements are marked by symbols (•). Theoretical spectra, calculated with quantum mechanics from the various models of β, are shown for comparison (curves). The inset of Fig. 2 represents the anisotropy as a function of separation in the restricted interval [3:6] bohr where overlap effects are particularly pronounced. The vertical line at $r \approx 4$ bohr indicates the minimum Ne-Ne distance effectively probed by the experiment at room temperature. The above-discussed SCF, CCSD, and CCSD(T) *ab initio* models are illustrated in ascending order. Focusing on the anisotropy's characteristic pattern around 4.5 bohr, enhancement of the bump is observed as one goes to higher and higher levels of optimization. For the sake of clarity, only the latest published model among the two available CCSD models is shown. The SCF model, whose bump is far less pronounced than it is in the other models, stands also far behind the others in terms of quality. When focusing on intensities, calculated spectra are seen to exhibit a similar trend producing in particular a saddle shape at the frequency where the same feature was observed experimentally. The agreement with observation gets steadily improved with increasing level of sophistication and becomes almost striking in the case of the CCSD(T) calculation. Particularly gratifying is the fact that this feature is reproduced qualitatively, as shown in Fig. 3, by a simple semiempirical model long ago suggested by Meinander, Tabisz, and Zoppi [15] (see also Fig. 10, therein). At that time, no emphasis had been placed on the aspect of that model spectrum in the far wing probably due to the lack of high-frequency experimental data [10]. A recent experiment by our group, dealing with atomic mixtures, revealed a similar feature in Ne-Ar, in agreement with quantum-mechanical spectra calculated on the basis of modern *ab initio* polarizabilities for that system [16]. As was pointed out therein, the saddle-shaped wing of Ne-Ar should be the reflection of the peculiar electronic structure of neon atom and its interactions, even though strongly attenuated (as compared to Ne-Ne) by the smooth signature of the heavy argon neighbor. Once again, the observed saddle in Ne-Ar should lie with the bump that characterizes at close separations the anisotropy of Ne-Ar [16].

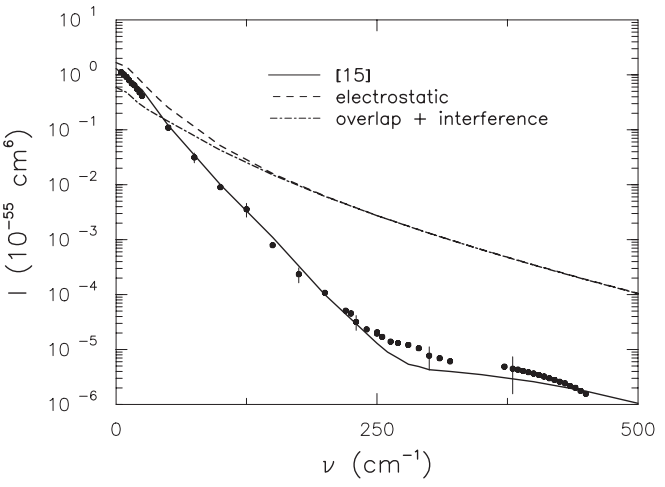

FIG. 3. Semiempirical Ne-Ne spectrum from Ref. [15] (solid line curve) along with spectra generated by long-range (electrostatic) polarization alone (dashed line curve) and by short-range overlap induction (dash-dotted line curve). The latter curve is illustrated with opposite sign since short-range effects contribute destructively. Our measurements are shown for comparison (•).

In pure neon, like in any atomic gas or mixture, spectral manifestations of short-range effects are expected to get more and more apparent as ν is increased. As shown in Fig. 3, the most transparent evidence of such effects is the substantial narrowing of the line shape as compared to spectral shapes generated by the long-range electrostatic induction alone. However, what is remarkable in the case of Ne-Ne is that, unlike any past studies with this gas or other atomic gases, electrostatic induction does not interfere regularly with orbital overlap. Owing to neon's structural specificity, tiny variations appear in the interference between the two mechanisms in the far wing of the Ne-Ne line shape. These variations, even though invisible on the scale of the figure (Fig. 3), greatly affect the spectrum, whose decay beyond 250 cm^{-1} slows down in a way unexpected for a typical atomic system. Thus, at 450 cm^{-1}, which is the upper frequency bound that was probed in our experiment, electrostatic spectrum is stronger by two orders of magnitude than the total Ne-Ne spectrum, but this difference would be further increased to five whole orders of magnitude if the Ne-Ne spectrum conserved all along the frequency range its near-exponential shape. These findings demonstrate the utility of low-noise Raman experiments as a probe very sensitive to even the slightest variations between competing polarization mechanisms as atoms interpenetrate.

In conclusion, this Brief Report is a contribution to the decades-long study of age-old issues. We studied the spectral response of the anisotropy of a pair of neon atoms via collision-induced Raman scattering by neon gas at room temperature. We provided evidence of the special way in which two neon atoms interact with each other at separations about half the typical size of neon atom. Our measurements almost tripled the spectral range hitherto explored. The huge extension into the spectrum revealed a well-defined saddle-shaped wing unique thus far in the area of collision-induced scattering by atomic pairs. It appears about 250 cm^{-1} away from the resonance frequency and is identically reproduced by large-scale *ab initio* computations. Its occurrence lies with a bump in the pair-polarizability anisotropy at close range separations shown to increase with the level of inclusion of electron correlation. This observation permits an advanced understanding of issues related to the interplay between long-range and short-range mechanisms and to the growing role of electron correlation close to the unified atom limit.

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