preceding discussion that the two-shell predictions are inadequate. An experimental determination of $\beta$ over the entire energy range from the 5s threshold to $\omega \simeq 2$ a.u. will provide a sensitive guide to relativistic atomic-structure theories.

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# Anomalous Behavior in the Vibrational Raman Spectrum of Oxygen under Near-Critical Conditions

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The isothermal density dependence of both the shift and width of the Raman $Q$ branch in oxygen gas have been found to exhibit anomalous behavior under near-critical conditions. The observed effects are interpretable in terms of moleuclar-cluster formation, and it is concluded that the Raman effect is a potentially valuable probe of density fluctuations in the critical region.

The density-dependent effects of intermolecular forces upon the vibrational Raman spectra of gases have been the subject of extensive experimental and theoretical work.[1] As a result, these effects are now fairly well understood for values of reduced temperature ($T/T_c$) greater than about 2. In the present context the essential points are (i) that at low densities the resolved structure of the pure vibrational Raman spectrum is characterized by frequency shifts which are predominantly linear in the density,[2] and (ii) that at sufficiently high densities this polarized $Q$ branch is subject to a narrowing process where the width varies as the inverse of the density.[3] In this Letter we present new experimental results for $O_2$ gas in the neighborhood of its critical point where the influence of density fluctuations may be responsible for departures in the behavior of the polarized spectrum from that expected on the basis of previous work. As a consequence we suggest that such experiments are capable of providing significant information regarding the nature of these fluctuations.

The data, which are presented graphically in Fig. 1, were obtained using previously described interferometric techniques.[4] The experimental errors in the determination of the relative frequency shift and the width are estimated to be ± 2% and ± 7%, respectively. Gas densities were determined using published $PVT$ data,[5] the absolute temperature and pressure being measured within limits of ± 0.02 K and ± 0.07 bar, respectively. It is recognized that the resulting uncertainty in the density may be considerable in the neighborhood of the critical density[6] (304 amagat). However, in this preliminary report we wish to emphasize the qualitative features of the observations, it being considered highly improbable that experimental errors could account for the anomalous, and quite reproducible, behavior which oc-

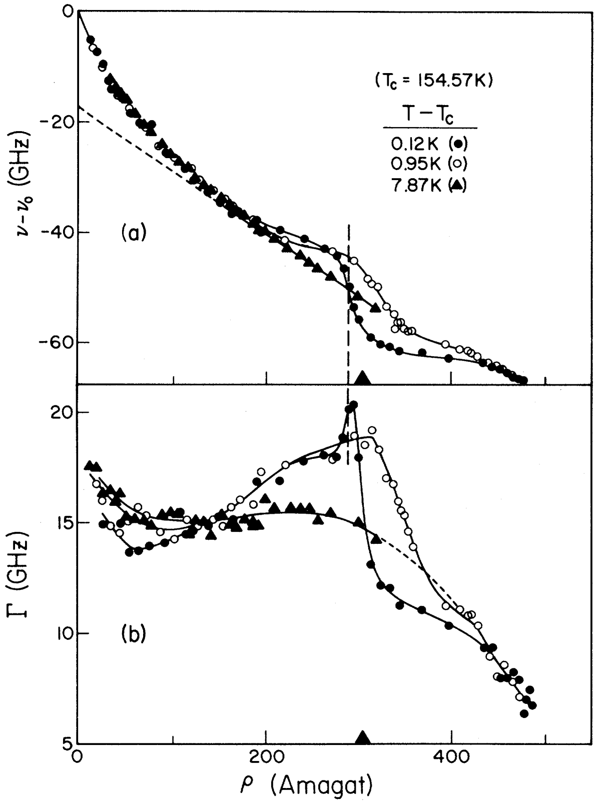

FIG. 1. High-resolution data showing the behavior of the Raman $Q$ branch of $O_2$ gas in the critical region ($\rho_c$ = 304 amagat). (a) The peak frequency shift relative to the value at zero density ($\nu_0$), as a function of density; (b) the full width at half-maximum, as function of density. Measurements were made using a scanning Fabry-Perot interferometer with a *spectral free range* of 110.7 GHz and a *finesse* of ~ 70. The maximum attainable density for $T - T_c = 7.87$ K was determined by the pressure limitations of the sample cell. See text for discussion of the linear extrapolation to $\rho = 0$ in (a).

curs for $T - T_c < 2$ K. This comment is directed in particular at the occurrence of a sharp maximum in the linewidth data of Fig. 1(b); such a phenomenon is not amenable to explanation in terms of possible gravity-induced density gradients, for example. In addition, we point out that considerable care was taken to ensure, insofar as possible, that equilibrium conditions were established for each measurement. Each pair of data points in Fig. 1 represents an average initial waiting period of ~ 1 h followed by a spectrum accumulation time of ~ 2 h.

The vibrational Raman frequencies, $\nu(\rho, T - T_c)$, are plotted relative to the value for $\rho = 0$ (which was obtained by extrapolation), the temperature dependence of the latter quantity being negligible over the ~ 8-K range so that $\nu(0, T - T_c) \equiv \nu_0$. As discussed below, the nonlinear behavior of the data at low densities ($\rho < 150$) is to be expected on the basis of known effects already treated in the literature; it is the nonlinear, dispersionlike behavior in the region $150 < \rho < 440$ which is of primary interest here. Figure 1(a) demonstrates the essential characteristics of this phenomenon; in particular, it is only readily observable for $T - T_c < 1$ K. A similar comment also applies to the linewidth data of Fig. 1(b): The broad maximum which occurs in the region $150 < \rho < 440$ for $T - T_c > 1$ K quite abruptly develops into a very sharp maximum for $T - T_c < 1$ K. The correlation between the behavior of the shift and width is also apparent, and a vertical dashed line has been drawn in Fig. 1 to emphasize this point for the case of $T - T_c = 0.12$ K.

Additional data not shown in Fig. 1 include a corresponding series of intensity measurements; and, in this connection, we emphasize an important characteristic of Fabry-Perot spectrometry as employed in these experiments: A spectral contribution whose width is greater by about an order of magnitude than the component being examined will occur only as a background level regarding which very little information can be extracted.[4] However, since the $Q$-branch scattering is highly polarized, it was readily verified that a substantial contribution to the $Q$-branch intensity was contained within the above-mentioned background. These measurements were performed under conditions of lowest practical resolution[7] with the scattered light restricted by filtering to a bandwidth of ~ 5000 GHz, centered at $\nu_0$. It is consequently concluded that the complete spectrum of the polarized Raman scattering includes not only the sharp component to which the data of Fig. 1 apply, but also a contribution whose width is greater by at least an order of magnitude. The intensity of the polarized background relative to that at the peak of the sharp component at $T - T_c = 0.12$ K was found to exhibit a distinct minimum in the same narrow density range where the corresponding width of Fig. 1(b) reached a maximum, i.e., for $\rho \simeq 290$.

Published data[2] for $H_2$ at 85 K, for example, show that the vibrational Raman shifts are proportional to density in the region $\rho < 300$ where the individual $Q$-branch components (of $H_2$) are well resolved. In the present case of $O_2$ the (zero-density) $Q$-branch structure is unresolvable and the departure from linear behavior for $\rho < 150$ is to be expected on the basis of current theories[3,8] of the particular *motional-narrowing* phenomenon which becomes important when the frequency of rotationally inelastic collisions is comparable (in appropriate units) to the vibration-rotation interaction energy. The narrowing which occurs with increasing density is accompanied by a change in the shape of the band from its characteristic asymmetrical form at very low densities[9] to a highly symmetrical form for $\rho > 150$. The shift in the peak frequency which is associated with the latter process is also responsible for the nonlinear behavior of $\nu - \nu_0$ in the region $\rho < 150$. It is to be noted that the shift data for $T - T_c = 7.87$ K exhibit the anticipated linear dependence on density for $\rho > 150$ and, as a matter of interest, Fig. 1(a) includes a linear extrapolation to zero density which, we feel, represents the direct effects of intermolecular interaction upon the $O_2$ vibrational frequency when critical effects are negligible.

Any interpretation of the previously described anomalous behavior must recognize the essential short-range nature of the intermolecular interactions involved. The range parameter is, in fact, of order 1 nm,[10] so that the density to which a single Raman-scattering event is sensitive should most appropriately be identified as a "local density," $\rho_{\text{loc}}$, corresponding to a volume element of ~ 1 $\text{nm}^3$, rather than the bulk density, $\rho$. Consequently, under near-critical conditions, one can sensibly expect that fluctuations in $\rho_{\text{loc}}$ will play a key role in accounting for the observed behavior of the Raman spectrum.

In the following discussion, attention is focused on the observations for $T - T_c = 0.12$ K and, for convenience, we define the quantities $\Delta\nu = \nu(\rho, 0.12) - \nu(\rho, 7.87)$ and $\Delta\Gamma = \Gamma(\rho, 0.12) - \Gamma(\rho, 7.87)$, which have positive and negative values throughout approximately the same density ranges, namely, $150 < \rho < 300$ and $300 < \rho < 440$, respectively. We associate fluctuations in $\rho_{\text{loc}}$ with the formation of molecular clusters, and suggest that a *cluster condensation* occurs near the critical density, $\rho_c$. The basis of our interpretation is the assumption that this cluster condensation can be characterized in part by a large and sudden change in the mean cluster lifetime, $\tau$. As a consequence, the sharp component which is observed in the high-resolution Raman spectrum behaves as a selective detector of (i) unclustered molecules in the $\Delta\nu > 0$ region and (ii) clustered molecules in the $\Delta\nu < 0$ region. This proposal and the ensuing ideas are, we feel, substantiated in an important way by the intensity measurements previously described.

At the low-density extreme of the $\Delta\nu > 0$ region, one can argue (i) that the fraction $n$, of $O_2$ molecules which occur in cluster form, as well as the size of any such clusters, will be small, and (ii) that $\tau$ may be comparable to the mean collision time. Under these conditions, any Raman scattering from clustered molecules will be weak and conceivably recognizable only as a background contribution to the high-resolution spectrum because of its large, lifetime-limited width. The sharp spectral component which is observed in this region can thus be associated with unclustered moelcules, and the principal (observable) effect of cluster formation will be the indirect one of giving rise to a *decrease* in the local density of these unclustered molecules. This, in turn, will give rise to observed relative Raman shifts which are lower in magnitude than those expected from a linear dependence on bulk density. If a small increase in $\rho$ is now associated primarily with an increase in $n$, there being no great change in $\tau$, the effect upon the shift will be enhanced so that the quantity, $\Delta\nu$, can be expected to increase in magnitude with a positive sign, as observed. As implied above, the cluster condensation may be regarded as reversing the roles of clustered and unclustered molecules due to a sharp increase in $\tau$; that is, for $\rho > \rho_c$, $n$ may approach unity and most of the molecules are presumed to occur in the form of relatively long-lived clusters of large size. The Raman scattering from unclustered molecules then becomes very broad and weak so that the observed component becomes, in effect, a probe of the internal cluster densities which, being higher than the bulk density, can account for the negative values of $\Delta\nu$. As the bulk density is further increased it will eventually approach the mean internal-cluster density at which point the effect should disappear, again in accordance with observations for $\rho \simeq 440$.

It has been demonstrated[4,8,11] that vibrational dephasing processes represent the most important contribution to the linewidth at the highest densities in the saturated liquid. In the present case, however, it is most probable that, of the processes which have been discussed in the literature, it is the motional-narrowing mechanism which is of greatest importance. Consequently, the width can be expected[3] to vary approximately as $\rho^{-1}$ when the density is sufficiently high so that the $Q$-branch profile is symmetrical, i.e., for $\rho > 150$ in the case of $O_2$. This behavior is obviously not reflected in the data of Fig. 1(b), but ideas already introduced are consistent with the observed behavior.

Given that in the $\Delta\Gamma > 0$ region it is the local density of unclustered molecules which should determine the width of the observed Raman line, then, because of its inverse density dependence, the linewidth should indeed be greater than expected on the basis of a bulk density calculation. However, this effect cannot account for the fact that $\Gamma$ exceeds its (extrapolated) zero-density value over a considerable part of this region, so that some additional contribution is apparently involved. In this connection, one can naively define a quantity $\tau'$ representing the average time during which a typical $O_2$ molecule is *not* part of a cluster. The equilibrium requirement, $n/(1-n) = \tau'/\tau$, then leads to $\tau' = (n^{-1} - 1)\tau$, whence it is apparent that $\tau'$ can be expected to *decrease* with with increasing $\rho$ in this region provided, *and as previously assumed,* that $n$ increases substantially with $\rho$ while there is no great change in $\tau$. Such a decrease in $\tau'$ may consequently account for the additional contribution to $\Gamma$.

The sharp decrease in linewidth which occurs near $\rho_c$ is clearly consistent with the presumed nature of the cluster condensation as already outlined. In addition, the existence of a $\Delta\Gamma < 0$ region is to be expected if the linewidth in this region is not limited by cluster-lifetime considerations. Such being the case, $\Gamma$ could be determined primarily by the (mean, internal) cluster density via the motional-narrowing process; i.e., the associated inverse density dependence together with a mean local density which is higher than the bulk value could give rise to negative values of $\Delta\Gamma$.

An additional interesting feature of the linewidth data of Fig. 1(b) is that an approximate $\rho^{-1}$ dependence is not apparent even at temperatures as high as $T - T_c = 7.87$ K, whereas $\nu(\rho)$ reverts to the expected linear behavior for $T - T_c > 2$ K. It seems reasonable to attribute the persistence of a broad maximum in $\Gamma(\rho)$ to the presence of small, residual clusters in the form of van der Waals molecules, which indeed can be expected to exist at even higher temperatures. If it is assumed that the fractional concentration of these van der Waals molecules is determined by temperature rather than density, while the converse is ture of their mean lifetime, then their manifestation via $\Gamma(\rho)$ is understandable within the framework of the ideas already advanced. It would therefore appear that it is the distinction between the processes of small- and large-cluster formation which is of essential importance here.

It should be emphasized that the segregation of molecules into two distinct species, namely, clustered molecules and other molecules, represents but an initial attempt to account for the gross features of the anomaly. It is hoped that a better understanding of the anomaly will result from experiments which are now in progress to examine more carefully the broad-band character of the polarized scattering using a grating spectrometer. These results, together with corresponding high-resolution data for $N_2$ and CO, will be presented in a more comprehensive publication to appear in the near future.

The experiments described here were undertaken following discussions with Professor H. L. Welsh, Department of Physics, University of Toronto, whose prior work with C. L. Jolliffe had demonstrated unusual behavior in the frequencies of $(\nu_1, 2\nu_2{}^0)$ Raman doublet of $CO_2$ under near-critical conditions. The authors are indebted to Professor Welsh for communication of these unpublished results and for continuing consultations.

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