

⁴He start from the many-atom wave function of Bijl-Jastrow form:

$$\Psi = \prod_{i < j} f(r_{ij}) \quad (3)$$

There can be no doubt from the work of McMillan⁷ that the "product of pairs" wave function (3) implies a condensate: i. e., the form (2) for $\gamma(r r')$ with $\rho_0 \neq 0$.

The work of Uang and Stwalley,¹ and of Skofronick,⁴ makes it unlikely that the wave function (3) can be realistic in liquid ⁴He at $T=0$ and reopens the interest in the properties of a wave function Ψ in which three-atom correlations (at least) are directly included. We know of no arguments presently that such a wave function, which, as March and Galasiewicz discuss, can imply superfluid-

ity, must also imply a Bose-Einstein condensate, its existence being a sufficient condition for superfluidity, not a necessary one.

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³See, for example, H. S. Huber and T. K. Lim, *J. Chem. Phys.* **68**, 1006 (1978).

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⁷W. L. McMillan, *Phys. Rev. A* **138**, 442 (1965); see also *Phys. Rev.* **175**, 266 (1968).

Comment on "The overtone spectrum of acetylene: A rotational analysis based on a local model description"^a

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In their recent article, Henry *et al.*¹ try to extend the local mode model to describe rotations. The work contains many errors and lacks adequate justification for the extensive approximations made. Some of the errors are discussed below.

(1) The theory begins with Watson's² Hamiltonian for a nonlinear molecule. However, as discussed by Watson,² this Hamiltonian is inappropriate for linear molecules. In particular, the term

$$U = -\frac{\hbar^2}{8} \sum_{\epsilon} \mu_{\epsilon\epsilon}$$

does not appear in the Hamiltonian for a linear molecule.³ It diverges as a molecule becomes linear. The nonlinear Hamiltonian should not be used for any molecular state that has an appreciable amplitude at the linear geometry. Even if acetylene has an effective nonlinear bending potential in excited stretching states, as the authors propose,⁴ the nonlinear Hamiltonian is still inappropriate.

(2) It is also claimed that: "Watson has shown that p_{ϵ} commutes with $\mu_{\epsilon\epsilon'}$ " (p_{ϵ} is the vibrational angular momentum $\mu_{\epsilon\epsilon'}$, the inverse moment of inertia tensor). In fact, what Watson² has shown is that $\sum_{\epsilon} [p_{\epsilon}, \mu_{\epsilon\epsilon'}] = 0$. The individual commutators are not zero.

(3) It states that the vibrational part of the Watson Hamiltonian is given by Eq. (4¹) neglecting "the small contribution of U ". In fact the vibrational term $\frac{1}{2} \sum_{\epsilon\epsilon'} p_{\epsilon} \mu_{\epsilon\epsilon'} p_{\epsilon'}$ has also been neglected.

(4) It states that for a local Morse potential function, the vibrational Hamiltonian may be expressed as given in Eqs. (5)–(8), but this only comes from Eq. (4) if the

bending degrees of freedom are dropped from the Hamiltonian. If they are not, then the G matrix will depend upon the bond coordinates.⁵

(5) The expression Eq. (16) given for the Hamiltonian matrix elements is incorrect.

(6) It is stated that "the vibration-rotation overtone bands of acetylene show Q -type transitions (Figs. 1 and 2) which indicates that the stretching motion of the C–H oscillators is coupled to the bending motion". In fact, a Q branch is only indicated in one of the figures, the $\Delta v = 2$ transition. Bend-stretch coupling cannot give the assigned transition a Q branch since vibrational interactions can only mix states of the same symmetry. The assigned upper state Σ_u can only interact with bending states of Σ_u symmetry. Therefore, the Σ – Σ character of the transition will not be altered. A Σ – Σ transition cannot have a Q branch, because of conservation of angular momentum. Even if the excited vibrational states of C_2H_2 are nonlinear, that would not change the qualitative selection rules. This can be seen by examining the UV spectrum of acetylene, which is to an excited electronic state with a nonlinear equilibrium. The rotational structure of each vibrational band can be understood in terms of linear molecule selection rules. The Q branch transitions reported by the authors will still be forbidden because $J \rightarrow J$, $K = 0 \rightarrow K = 0$ transitions are forbidden for an asymmetric top. The transition must be $K = 0 \rightarrow K = 0$ because if it were not, it would not show intensity alternation.

(7) It is argued that only the *cis* bend need be considered in bend-stretch interactions because "the vibrationally induced dipole moment for the *cis*-bending

configuration will be far larger than for the other two configurations". These interactions are mechanical; the bending degree of freedom does not need a vibrationally induced dipole moment in order to interact with stretching degrees of freedom, which for CH overtones carry the intensity.

(8) The model neglects all potential coupling between the oscillators, even though the force field of Strey and Mills⁶ indicates that such couplings are not negligible.⁷ It then uses the experimentally observed splitting to fix ρ , the effective *cis* bend angle, for the excited states. Given the approximations, this choice of ρ has no physical significance. Recent large basis set variational calculations by Halonen, Carter, and Child⁸ have shown that the vibrational states of C₂H₂ and C₂D₂ can be fit to a simple four free parameter linear potential (Morse oscillators with harmonic coupling) with standard deviations of 6 and 3 cm⁻¹, respectively. Given that the Q-branch assignment is wrong, there is no reason for introducing the ρ coordinate at all.

(9) The experimental data presented for $\Delta v = 2, 3$ is useless, since much higher quality data was previously reported.⁹ It is claimed that the $\Delta v = 2$ band has a Q branch at 6561.1 cm⁻¹, but the previous work put the origin at 6556.461(2) cm⁻¹. Of this " $\Delta v = 2$ Q branch" it is stated that Herzberg¹⁰ suggested it is a difference band. On pages 290 and 291, Herzberg lists "all the infrared and Raman bands" of acetylene, and no difference band is listed anywhere close to 6000 cm⁻¹. In the high resolution spectra⁹ no transition with a Q branch is listed at 6561 cm⁻¹. In fact, the published high resolution spectrum shows two strong features near the origin of the $\Delta v = 2$ band. They are the R(11) line of $v_1 + v_3 + v_4^1 - v_4^1$, and the R(9) line of $v_1 + v_3 + v_5^1 - v_5^1$ sequence band transitions. The spectrum shows that these transitions have intensity comparable to R(0) of the $\Delta v = 2$ ($v_1 + v_3$) transition.

(10) The authors claim to analyze their spectra ignoring *l*-type doubling. Since the transition that they are looking at shows intensity alternation, it can not have unresolved *l* doubling.

(11) It is claimed that the intensity anomaly observed in the P branch of $\Delta v_{\text{CH}} = 2$ is due to a transition to the (0, 2)₊ state. Such a transition from the ground state is forbidden by dipole selection rules ($g \rightarrow g$). The level (2, 0)₊ of a nonlinear C₂H₂ could only have a perpendicular transition moment from the ground state. Such a transition moment could only induce $\Delta K = \pm 1$ rotational transitions. Looked at from the basis set of a linear molecule, such a transition will be assigned as a combination band of (2, 0)₊ with a quantum of Π_u bend. This level has been reported⁹ and has a vibrational term value of 7219.37 cm⁻¹. A transition from the ground state to this level cannot occur near 6500 cm⁻¹. The "intensity anomaly" is shown by the previous spectrum to be due to the $\Pi_g \rightarrow \Pi_u$ $v_1 + v_3 + v_5^1 - v_5^1$ [6534.742(4) cm⁻¹] and the Π_u $\rightarrow \Pi_g$ $v_1 + v_3 + v_4^1 - v_4^1$ [6529.800(4) cm⁻¹] sequence bands, red shifted from the ground state transition.⁹ The published spectrum shows 18 resolved rotational bands in this energy region. None of these bands, which include many weak bands from excited vibrational states with

1500 cm⁻¹ of energy, have an origin of 6502.30 cm⁻¹ which is the observed vibrational term value of the (2, 0)₊ ($2v_3$) energy level.^{9,11} The transition observed with an origin of 6502.389(6) cm⁻¹ cannot be to this level, as combination differences shows that the lower state of this reported transition is not the ground state.

(12) In choosing parameters for the model for the rotational constants, the values of one C-H and the C-C bond lengths were fixed at 1.056 and 1.204 Å, respectively. For the ground state, the other C-H bond length is calculated to be 1.094(4) Å. No comment is made upon the fact that it is predicted that the ground state of C₂H₂ has C-H bond lengths differing by 0.04 Å.

(13) It is stated that "the results for the $\Delta v = 5$ are puzzling, there is an apparent reduction in R_2 for the ground state... It is difficult to ascribe these irregularities to uncertainty in the data... It is therefore tempting to search for a physical cause for such an anomaly". The reduction in R_2 comes from a discrepancy in B'' for this band. If the lower state rotational constant was really different in this band, that would be proof that the transition did not originate in the ground state of acetylene. The only cause for such an anomaly would be a misassignment. Recent high resolution work by us¹² has shown that ground state combination differences from the $\Delta v_{\text{CH}} = 5$ and 6 transitions can be fit to ~ 0.001 cm⁻¹ using the literature values for the ground state rotational constants. The data for the $\Delta v = 5$ band used in the article was published in 1932, when accurate ground state B values were not yet known.

(14) The vibrational dependence of rotational constants is much more complex than just changes in average position. In particular, the vibrational average of a function of a coordinate is not just the function evaluated at the average position, as Henry *et al.* have assumed in Eqs. (17), (19), and (20). No attempt was made to justify these approximations. In addition, if the vibration-rotation interaction constants σ_i are computed for the two C-H stretching vibrations from the Strey and Mills⁶ anharmonic force field, approximately 50% of their magnitude comes from Coriolis coupling. Therefore, the interpretation of the change in B as a geometric effect alone is incorrect.

(15) There is much experimental evidence to discount the claim that excited vibrational states of acetylene have a significantly nonlinear equilibrium. Such an assumption would imply that the bending vibrations are drastically changed upon excitation of the stretching vibrations. One bending degree of freedom would become a rotation, and the degeneracy of the other broken. Many excited vibrational states with both stretching and bending excitation are known, and no such anomalous behavior is observed.

(16) The authors reply⁴ reports new values for ρ that invalidate an important assumption made in the analysis of the observed rotational constants.

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Reply to Comments of Lehmann, Scherer, and Klemperer

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The primary purpose of our recent paper on the overtone spectrum of acetylene¹ was to demonstrate that the most natural and effective starting point for the description of the spectrum was in terms of the local mode model. A secondary purpose was to point out the presence of extensive bending stretching interaction and to attempt a first step at understanding this difficult problem. In their recent paper on the $\Delta v_{\text{CH}} = 5$ and 6 overtone transitions in acetylene and isotopically substituted acetylenes,² the authors of the comment appear to reach substantially the same overall conclusions, i.e., "... vibrational term values cannot be explained in terms of the usual slightly anharmonic normal mode expansion... the simple local mode theory... can be used to rationalize many aspects of the spectrum..." and "An interesting question raised by this work concerns the nature of the interaction between bending and stretching degrees of freedom for these highly excited states. Our understanding of these bend-stretch interactions is hampered by our lack of a theoretical model..."²

With regard to the specific points raised in the comments:

(1) It is true that we have used Watson's Hamiltonian for a nonlinear molecule. However, in reducing the Hamiltonian, we have used the method described by Sørensen³ which uses a different choice of coordinates

than Watson.⁴ Under these conditions, as demonstrated by Sørensen,³ the resultant Hamiltonian can be applied to both linear and nonlinear cases.

(2) This is a valid comment. However, due to our neglect of the terms $(1/2) \sum_{gg'} p_g \mu_{gg} p_{g'}$ (see reply to comment 3), the absence of the summation sign for the commutator has no effect on our results.

(3) It is true that the vibrational term $(1/2) \sum_{gg'} \times p_g \mu_{gg} p_{g'}$ has been neglected. Such a term did not provide any additional information at the level of analysis conducted in our paper.

(4) Lawton and Child⁵ have shown that in water, inclusion of the bending vibration reduces the mean energy of the overtone transition but has little effect on the splittings between the + and - local mode states, and thus inclusion of the bending vibration does not effectively change the local mode spectral pattern. For this reason we have not included the bending degrees of freedom in our local mode Hamiltonian.

(5), (8), (17). We agree that Eq. (16) is incorrect. The off diagonal matrix elements of the operator $C[C = -\hbar^2 G_{ij}^0 (\partial^2 / \partial R_{\text{CH}} \partial R_{\text{CC}} + \partial^2 / \partial R_{\text{CC}} \partial R_{\text{CH}})]$ can be simplified following the same procedures as Child and Lawton.⁶ Thus, to second order, this matrix element, in terms of the local mode frequency ω , is given by

$$\langle v_i' v_j' v_C(=0) | C | v_i v_j v_C(=0) \rangle = -7.8128 \times 10^{-4} f_2 \left[\left(1 + \frac{m_C}{m_H} \right) x_{\text{CH}} x_{\text{CC}} \right]^{-1} [M(s_{\text{CH}}, v_{\text{CH}} = v_i + 1) M(s_{\text{CH}}, v_{\text{CH}} = v_i) \\ \times \delta_{v_i', v_i+2} O(s_{\text{CH}}, v_{\text{CH}} = v_j - 1) O(s_{\text{CH}}, v_{\text{CH}} = v_j) \delta_{v_j', v_j-2} + M(s_{\text{CH}}, v_{\text{CH}} = v_i) \delta_{v_i', v_i+1} O(s_{\text{CH}}, v_{\text{CH}} = v_j) \delta_{v_j', v_j-1}] .$$

Due to the error, the angles quoted in the paper are incorrect. The correct values are $\rho = 35^\circ$ for $\Delta v_{\text{CH}} = 1$ and $\rho = 43^\circ$ for $\Delta v_{\text{CH}} = 2$. The ρ values now follow the opposite trend to that previously observed. As we have noted in the paper, these angles are very sensitive to the model and are too large due to our neglect of potential energy coupling. We expect that inclusion of the potential energy coupling would lower the ρ values suf-

ficiently for the diatomic molecule approximation to be still valid.

With regard to the recent calculations of Halonen *et al.*,⁷ the reported standard deviation of 5.6 cm^{-1} reflects the quality of the overall fit. This averaged value masks the larger deviations observed for transitions to some of the pure CH-stretching overtone states. Even