

Lawrence Berkeley National Laboratory

Recent Work

Title

NEW ASPECTS OF BUFFER GAS EFFECTS IN RESONANT SPECTROPHONES

Permalink

<https://escholarship.org/uc/item/8t53z403>

Author

Johnson, R.H.

Publication Date

1981-06-01

c.2



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

ENERGY & ENVIRONMENT DIVISION

APR 10 1981
LIBRARY AND DOCUMENTS SECTION

To be presented at the 2nd International Photoacoustic Spectroscopy Conference, Lawrence Berkeley Laboratory, University of California, Berkeley, CA, June 22-25, 1981

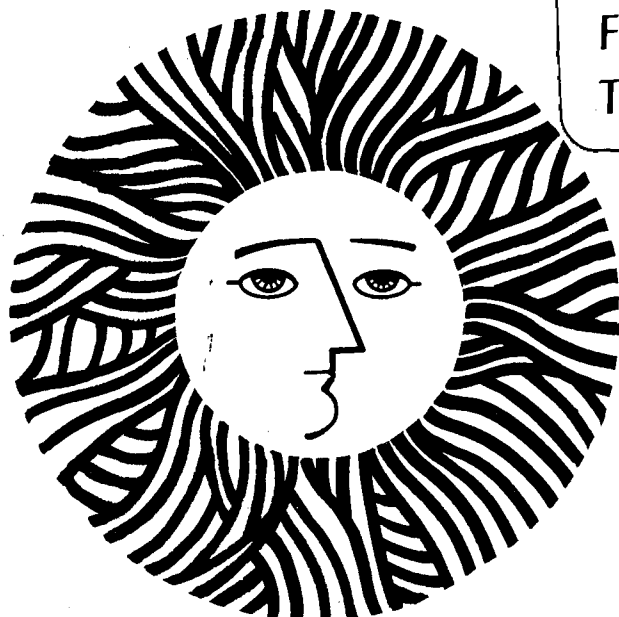
NEW ASPECTS OF BUFFER GAS EFFECTS IN RESONANT SPECTROPHONES

Ralph H. Johnson, Launey J. Thomas III, Robert Gerlach, and Nabil M. Amer

June 1981

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 6782



LBL-12367
c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

NEW ASPECTS OF BUFFER GAS EFFECTS
IN RESONANT SPECTROPHONES

Ralph H. Johnson, Launey J. Thomas III, Robert Gerlach
and Nabil M. Amer

Applied Physics and Laser Spectroscopy Group
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720
U.S.A.

Abstract

Pressure dependent spectrophone Q's and frequency shifts were measured for 11 buffer gases and explained in terms of classical boundary layer effects and molecular relaxation.

This research was supported by the Assistant Secretary for Environment, Pollutant Characterization and Measurement Division of the U.S. Department of Energy, under contract No. W-7405-ENG-48.

NEW ASPECTS OF BUFFER GAS EFFECTS

IN RESONANT SPECTROPHONES

Ralph H. Johnson, Launey J. Thomas III, Robert Gerlach
and Nabil M. Amer

Applied Physics and Laser Spectroscopy Group
Lawrence Berkeley Laboratory
Berkeley, CA 94720
U.S.A.

In studies of gas phase photoacoustic spectroscopy, the gas whose spectrum is being investigated is generally one of several present in the sample, and often only in trace amounts. The response of the spectrophone is determined by the characteristics of the sample gas as a whole, and depends on the various thermal and molecular relaxational properties of the gases present. In particular, for an acoustically resonant spectrophone, important characteristics will include the sound velocity, heat capacity, thermal conductivity, viscosity, and the energies and relaxation times of the molecular vibrations. The sound velocity determines the resonant frequencies of the cavity, while the other parameters govern the loss mechanisms that determine the quality factors of the resonances, and also cause small shifts in the resonant frequencies. In an earlier study,¹ the resonant frequencies and quality factors of acoustical resonances were determined for various buffer gases at atmospheric pressure, and the results were compared to theoretical predictions² based on classical surface viscous and thermal losses. Significant discrepancies were observed for all non-noble gases.³ It is the goal of this work to investigate the pressure dependent behavior of the spectrophone, and to incorporate molecular relaxation effects into the theoretical interpretation of that behavior. We have made a number of extensions and improvements in experimental and analytical technique. The spectrophone used was a stainless steel cylinder polished to a 1/3 micron surface finish to guarantee well defined boundary layers whose losses could be calculated accurately from theory. The spectrophone and vacuum system were bakeable to reduce impurity effects due to outgassing. Whereas in the earlier experiment a large concentration of the optically absorbing component (9000 ppm of CH₄) was used, we kept the absorber concentration small

(50 ppm of C_2H_4) so as not to disturb the properties of the buffer gas. Use of an electro-optic modulator system allowed access to modes at much higher frequencies, thus enabling the study of lighter gases. We have measured the resonant frequency and quality factor as a function of pressure from atmospheric pressure down to 10 torr or lower for each buffer gas. Data analysis consisted largely of nonlinear least squares curve fitting of the resonant response curves, which gave more accurate determinations of the resonant frequency and Q than the half power point method used in the previous experiment.

Buffer gases studied included monatomic (He, Ne, Ar, Kr, Xe), diatomic (H_2 , N_2 , O_2) and polyatomic (CO_2 , N_2O , SF_6) gases. In all cases except SF_6 (which is already a strong absorber), 50 ppm of C_2H_4 was added to provide optical absorption at CO_2 laser wavelengths. For each gas, the Q and resonant frequency of the first radial mode were determined as a function of pressure, and the Q 's and frequencies of other modes were determined at atmospheric pressure; in some cases, other modes were also studied at sub-atmospheric pressures. The resulting data on f_{res} and Q vs. pressure were compared to theoretical curves generated by summing the surface viscous and thermal losses, the bulk viscous and thermal (Stokes-Kirchhoff) losses, and the losses due to molecular relaxation effects. For the latter it was assumed that all vibrational levels relaxed with a single relaxation time which was adjusted to give the best fit to the data.

It was found that for monatomic gases, the classical surface losses accounted almost entirely for the observed Q factors at all pressures. For the diatomic molecules N_2 and O_2 the relaxation times are so long that they do not produce much relaxational damping at or below atmospheric pressure and the classical surface losses again largely account for the observed Q . For H_2 , the vibrational energy is so high that the acoustic wave does not significantly excite molecular vibrations, but it is necessary to include rotational relaxation to explain the observed Q 's. For polyatomic gases, we found that the observed pressure dependence of Q could be well explained by the combined effects of classical losses plus vibrational relaxation, provided the assumed relaxation times were adjusted to fit the data.

It has already been pointed out⁴ that molecular relaxation effects will also give rise to a frequency shift as a function of pressure. However, even

for monatomic gases, for which molecular relaxation effects should be absent, we observed pressure-dependent frequency shifts. For all of the noble gases, we observed a downward shift in frequency at low pressure which appeared consistent with a $p^{-1/2}$ pressure dependence. We interpret this as being due to a reduction in the speed of sound in the thermal boundary layer, whose thickness varies as $p^{-1/2}$. The gas in this layer is in good thermal contact with the walls, and hence sound propagation is no longer adiabatic, as in the bulk of the gas, but tends toward isothermal behavior as one approaches the wall. We have calculated to first order that the frequency shift is

$$\left(\frac{\delta\omega}{\omega}\right)_{bl} = d_h \left(\frac{1}{L} + \frac{1}{R}\right) \left(1 - \sqrt{\gamma} - \frac{1}{2} \ln \gamma\right) \quad (1)$$

where $d_h = (2\kappa/\omega \rho C_p)^{1/2}$ is the thermal boundary layer thickness, L and R are the cell length and radius, and $\gamma = C_p/C_v$. This is reasonably consistent with observed frequency shifts.

For Xe, we also observed a downward shift in frequency with increasing pressure above ~ 100 torr. This shift is accounted for by a change in the speed of sound due to deviation of the equation of state from that of an ideal gas, and is given by

$$\left(\frac{\delta\omega}{\omega}\right)_{vir} = \frac{p}{R_g T} \left(B + \frac{T}{h} \frac{dB}{dT} + \frac{T^2}{2h(h+1)} \frac{d^2B}{dT^2} \right) \quad (2)$$

where B is the second virial coefficient, $h=C_v/R_g$, and R_g is the gas constant.

Having accounted for these shifts, which may be present for any gas, we next proceed to the relaxing gases. The diatomic gases produced no observable relaxational frequency shifts in the pressure range of our experiment. For the polyatomics, the frequency vs. pressure data could be fitted with theoretical curves by assuming a single effective relaxation time. The times thus arrived at are consistent with those obtained from the dependence of Q on p.

One other interesting effect observed was a coupling between modes due to boundary layer effects. Although the gas absorbed too weakly to allow direct excitation of modes having longitudinal dependence, these could be indirectly excited in cases where they were nearly degenerate with radial modes. We believe this is due to a coupling between these modes caused by viscous effects on the end walls. Isolated longitudinal modes, far from any radial modes, are never observed (except for the strong absorber SF_6).

In conclusion, we have gained some insight into the physics of resonant spectrophones. This should be useful in their application over a wide range of pressure and with a wide variety of buffer gases, and potentially also in the determination of molecular relaxation times.

We are grateful to Kenneth Jackson for his help in this experiment. This research was supported by the Assistant Secretary for Environment, Pollutant Characterization and Measurement Division of the U. S. Department of Energy, under contract No. W-7405-ENG-48.

References

1. L. J. Thomas III, M. J. Kelly, and N. M. Amer, Appl. Phys. Lett. 32, 736 (1978)
2. R. D. Kamm, J. Appl. Phys. 47, 3550 (1976)
3. In Reference 1, Table I, the ratio $Q_{\text{exp}}/Q_{\text{cal}}$ was based on incorrectly calculated values of Q_{cal} . The $Q_{\text{exp}}/Q_{\text{cal}}$ column should read: Ne, 0.87; Ar, 0.77; Kr, 0.82; Xe, 0.76; CO, 0.73; N₂, 0.82; ¹²CO₂, 0.15; N₂O, 0.36; SF₆, 0.44.
4. K. Frank and P. Hess, Chem. Phys. Lett 68, 540 (1979)

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720