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Detection and discrimination of pure gases and binary mixtures using a single microcantilever

A. Loui*, D.J. Sirbuly*,¹, S. Elhadj, S.K. McCall, B.R. Hart, T.V. Ratto

Lawrence Livermore National Laboratory, 7000 East Ave., Livermore, CA 94550, USA

(Received:

* Corresponding author. Tel.: +1 925 422 2840; fax: +1 925 422 3160

** Co-corresponding author. Tel.: +1 858 822 4143; fax: +1 858 534 9553

E-mail addresses: loui2@llnl.gov (A. Loui),

dsirbuly@ucsd.edu (D. J. Sirbuly).

¹ Present address: Department of NanoEngineering, 9500 Gilman Dr., La Jolla, CA 92093, USA.

Abstract

A new method for detecting and discriminating pure gases and binary mixtures has been investigated. This approach combines two distinct physical mechanisms within a single piezoresistive microcantilever: heat dissipation and resonant damping in the viscous regime. An experimental study of the heat dissipation mechanism indicates that the sensor response is directly correlated to the thermal conductivity of the gaseous analyte. A theoretical data set of resonant damping was generated corresponding to the gas mixtures examined in the thermal response experiments. The combination of the thermal and resonant response data yields more distinct analyte signatures that cannot otherwise be obtained from the detection modes individually.

Keywords: gas detection; cantilever sensor; piezoresistive; thermal conductivity; resonant damping

1. Introduction

Piezoresistive microcantilevers have been widely used in micro-electro-mechanical systems (MEMS) sensor arrays for the detection of chemical vapors and gases, where the embedded signal transducer (the piezoresistor) provides a more compact, rugged, and low-power alternative to the optical feedback mechanisms inherited from atomic force microscopy [1-9]. As a platform for sensing the vapors of liquid chemicals [1, 2, 5, 6] or the sublimates of solids [4, 7], piezoresistive cantilevers are typically coated with chemically functionalized materials with some affinity for the gas-phase species of interest (i.e., the analyte). The chemical interaction between the analyte and sensing material creates a bending response and concomitant piezoresistive change in the cantilevers that is readily measured.

MEMS-based sensing of chemical species that are gases at typical temperature and pressure conditions of interest (e.g., ambient atmospheric) is much more difficult. First, many gases under such conditions have little thermodynamic tendency to partition into the bulk of common sensing materials (e.g., polymers); this is the result of low cohesive energy densities and hence small solubility parameters, particularly for non-polar gases. Second, since chemisorptive interactions are usually exploited as a means of detecting and discriminating gas-phase analytes, highly inert species such as N_2 and the noble gases are virtually undetectable by sensors using chemically functionalized materials (e.g., alkanethiol self-assembled monolayers). For reactive gases, various strategies based on metals or metal/polymer composites have been successfully demonstrated with cantilever-based sensors; these include the use of palladium in sorptive coatings for hydrogen detection [10-12], a nickel salt/polymer composite as a catalyst for carbon monoxide sensing [3], and colloidal gold in keratin to detect hydrogen cyanide [8].

Alternatively, approaches that rely on the physical properties, rather than the chemical bonding characteristics, of gas analytes can remedy these difficulties. For comparative purposes, it serves to examine two gas detection methods that are amenable to hand-portability – a major criterion for modern sensor platforms intended for field use. Conductometric sensors, which represent the oldest and most widespread type of gas detector, are based on measuring changes in the conductance of a semiconductor (most commonly tin dioxide) upon reaction of reducing gases with adsorbed oxygen anions. The practical limits of detection (LOD) for commercial sensors of this type approach the low parts-per-million (ppm) range. As an example, the TGS 3870 (Figaro Engineering, Inc.) has a reported limit of 50 ppm for carbon monoxide, but requires operation at temperatures above 200°C [13].

Pellistors constitute a major class of electrical gas sensors which are calorimetric in nature. Catalytic pellistors measure the heat evolution from catalytic oxidation of the gas analyte, and are the most common commercial type [14-17]. Another pellistor variant relies on the measurement of heat dissipation into the gas analyte [16, 18, 19]; this approach, which seeks to identify gases based on their thermal conductivity, is based on the same principles as those described later in this paper in the context of a cantilever-based sensor (Section 3). In each case, a characteristic property of the gas (combustion enthalpy or thermal conductivity, respectively) creates a temperature change that can be measured resistively – either by a platinum resistance temperature detector or a thermistor. The LOD for commercial sensors of this type are typically in the low parts-per-thousand (ppth) range (e.g., VQ series pellistors from e2v technologies), although the catalytic types must operate at combustion temperatures of about 500°C [20].

While conductometric and calorimetric types of gas sensors can typically detect gases at meaningful concentration thresholds (e.g., below the lower explosive limit for combustible

gases), they generally suffer from deficiencies in selectivity – that is, in the ability to discriminate gases from one another. This poor discrimination originates in the fundamental physical mechanisms of each detection approach; for conductometric sensors, multiple gases may reduce the adsorbed oxygen anions similarly; for calorimetric sensors, many pure gases (or mixtures thereof) may have similar combustion enthalpies or thermal conductivities. The resulting sensor responses have an inherent ambiguity, and cannot serve as unique identifiers or signatures for the analytes except in applications where the gas constituents are of limited number and known to have sufficiently dissimilar physical characteristics.

The concept of combining gas sensing modalities to increase discrimination has been extensively explored by Göpel et al. (see Ref. [21] for an excellent overview) and examined more recently by Hierlemann et al. [22, 23]. This multimodal approach relies on the combination of sensing approaches that each have a broad cross-reactivity (i.e., respond, not necessarily uniquely, to multiple analytes), but which generate sets of response data that have a substantial degree of mutual orthogonality resulting from the fundamental differences between sensing principles. The combined multimodality data may therefore provide more distinct analyte signatures that cannot otherwise be derived from the separate detection modes.

In this paper, we describe a new method for detecting and discriminating gases that combines two distinct physical mechanisms within a single piezoresistive microcantilever: 1) heat dissipation; 2) resonant damping in the viscous regime. Experimental data are presented which demonstrate the sensor response to changing conditions of heat dissipation that are directly attributable to the thermal conductivity of the gas. By computing the theoretical shifts in cantilever resonant frequency resulting from viscous gas damping, and combining this simulated data with the experimental heat dissipation data, we show that a hypothetical dual-

modality cantilever sensor can achieve vastly improved gas discrimination compared to the modalities operating separately.

2. Experimental

The gas sensing experiments were performed using a hand-portable, piezoresistive cantilever array sensor previously developed for the detection of chemical vapors, including chemical warfare agents; a description of this work, including the sensor platform, is provided in Ref. [9]. In the current study, gases are identified based on their thermal conductivity rather than on their potential chemical bonding properties, so cantilevers devoid of functional polymeric coatings – and hence, operationally identical – were utilized. The piezoresistance signals from eight cantilever channels were measured to ensure full redundancy in the sensor response. A schematic diagram of the circuit is shown in Fig. 1.

Eight representative gases were selected to demonstrate the heat dissipation sensing concept, along with N₂ as a common diluent in binary mixtures. These ultrahigh purity gases were purchased commercially from various sources: 1) Ar, CO₂, and N₂ from Air Liquide America (Houston, TX, USA); 2) He, H₂, Ne from Matheson Tri-Gas (Parsippany, NJ, USA); 3) Kr from Airco (Santa Clara, CA, USA); 4) CH₄ from Air Products (Allentown, PA, USA); 5) Xe from Airgas (Radnor, PA, USA).

A custom gas mixing system was used to prepare the binary mixtures with N₂ (Fig. 1). Concentrations of each gas mixture between zero (pure N₂) and 100% (pure gas) were obtained by a simple two-channel mixing based on relative flow rates. Gas temperatures were measured by a K-type thermocouple inserted into the mixed gas flow approximately 15 cm upstream of the sensor inlet. Total flow rates between 18 and 90 standard cubic centimeters per minute (sccm)

were measured downstream of the sensor exhaust outlet using an ADM2000 flow meter from Agilent Technologies (Santa Clara, CA, USA). All experiments were conducted at ambient atmospheric pressure.

3. Thermal conductivity based sensing

The basic sensing principle involving heat dissipation, as embodied by a piezoresistive microcantilever, is simple: as the gaseous environment becomes more or less conductive to heat, the electrically-powered “self-heated” piezoresistor decreases or increases its temperature, respectively. Since the piezoresistor is a doped semiconductor, its resistance R_c depends on its temperature T_c in a characteristic manner. Therefore, measurement of R_c provides information about the thermal conductivity of the gas and hence the identity of the gas.

We previously developed a closed form model to describe the thermal response behavior of piezoresistive cantilevers in gaseous environments with potentially varying thermal conductivity, temperature, and flow rate [24]; this model successfully predicted the thermal drift in field data obtained with the cantilever array sensor described in Ref. [9]. In the prior work, calculations revealed that the piezoresistive response $\Delta R_c/R_c$ to gases in a constant temperature environment was dominated by thermal conductivity changes, with concomitant bending contributions induced by changes in T_c nearly three orders of magnitude smaller [24]. Although changing environmental temperatures will create additional contributions to $\Delta R_c/R_c$ independently of the gaseous thermal conductivity, these effects can be ignored in the present study as a result of the isothermal experimental conditions.

The thermal conductivities k of the nine gases examined in the current study are listed in Table 1. For the piezoresistive cantilevers employed in this work, the boron dopant is implanted

at an approximate dose of $5 \times 10^{15} \text{ cm}^{-2}$ [25]; this dopant level is sufficiently high that hole-phonon scattering dominates over the effect of increased carrier concentration from thermal promotion to the conduction band [26]. Thus, the overall effect is an increase in resistance with an increase in temperature (i.e., a positive temperature coefficient of resistance), with a high degree of linearity in the 250 to 800 K range [26, 27].

Using the resistance corresponding to 70 sccm of N_2 flow at 298 K as a baseline reference, the cantilever piezoresistance change ΔR_c vs. percent composition for eight binary gas mixtures (N_2 with test gases Xe, Kr, CO_2 , Ar, CH_4 , Ne, He, or H_2) was measured experimentally (Fig. 2) and the data represent averages taken over the eight cantilever channels. The heat dissipation sensor exhibits a linear response to increasing test gas content with respect to the N_2 diluent, and achieves a maximum stable value within one to two minutes. Since ΔR_c depends on the relative differences in heat dissipation between each gas and N_2 , those gases with smaller k than N_2 cause the embedded piezoresistor to increase in temperature and correspondingly in resistance; conversely, gases with a larger k lead to a decrease in resistance. These behavioral trends can be observed in Fig. 2.

The cantilever temperature as a function of gas composition was determined from a resistance vs. temperature calibration obtained in our previous study [24]. The operating temperature under the baseline reference condition (70 sccm of N_2 flow at 298 K) was 306 K, with maximum temperature excursions of several Kelvin for the most thermally insulative (Xe, at +2.5 K) and conductive (H_2 , at -2.5 K) pure gases. Note that the operational temperatures for the cantilever gas sensor are significantly lower than those required for conductometric and catalytic calorimetric detectors (500 – 800 K). The temperature changes ΔT_c vs. composition are also shown in Fig. 2 to provide a direct comparison to the corresponding piezoresistance

changes. By comparing the magnitudes of ΔR_c to ΔT_c as a function of gas composition, it is clear that the heat dissipation mechanism can be a sensitive means of gas detection. For example, an increase in Ar content from 0 to 9.9% for an Ar/N₂ mixture leads to a 40 mK increase in T_c and a $\sim 0.4 \Omega$ increase in R_c ; this change in resistance is readily measured by the Wheatstone circuit, which possesses a noise-limited detection threshold of $\sim 30 \text{ m}\Omega$. Applying linear scaling as observed in Fig. 2, the projected LOD of the current heat dissipation sensor for the test gases is a few ppth; these values are comparable to the detection limits of commercial catalytic pellistors, although we note that such sensors can only detect flammable gases below their lower explosive limits and not inert gases such as argon [20].

If the minimum detectable ΔR_c could be reduced to less than $1 \text{ m}\Omega$, a LOD in the 100 ppm range would be achieved (e.g., 200 ppm of Ar in an N₂ background at $0.8 \text{ m}\Omega$ resolution). Such a LOD is comparable to that obtained with commercial conductometric sensors, although this detector type is designed for reducing gases and, like catalytic pellistors, is insensitive to inert gases [13]. One strategy that can greatly improve the sensitivity of the thermal conductivity cantilever sensor is to go from a direct-current (dc) mode of detection, with a steady-state input bias and output signal amplifier, to an alternating-current (ac) mode using a periodic input voltage and lock-in amplifier. For example, a 20-fold improvement in temperature resolution for piezoresistive cantilevers using an ac vs. dc approach has been reported by Corbin et al. for an optimized measurement frequency of 10 kHz [28]. In addition, a judicious choice of integration time constant with respect to the data sampling rate should also aid in the reduction of noise.

The noise-limited detection threshold ($30 \text{ m}\Omega$) excludes significant thermal drift effects, since the gas exposure experiments were performed under practically isothermal conditions. From a prior study, in which the cantilever sensor was operated under ambient outdoor (“field”)

conditions, we have observed environmental temporal temperature gradients of up to ~ 2 mK/s during afternoon sun exposure leading to thermal drift of nearly 3Ω [24]. Such an effect could completely mask the appearance of a gas to the sensor – for example, a small Ar leak that coincides with a particular drop in temperature. Since the underlying mechanism of detection is thermal in nature (i.e., heat dissipation), any drift compensation method must distinguish the desired ΔR_c changes due to gas thermal conductivity from those associated with changes in environmental temperature. A closed-form model, with the ambient temperature as the sole variable input, was used to simulate the thermal drift of a field-deployed piezoresistive cantilever sensor [24]. Such a model can be readily integrated into the data acquisition software to provide active drift compensation, provided accurate measurements of the gas temperature near the cantilever are made simultaneously.

4. Gas discrimination using dual sensing modalities

The inherent ambiguity in the heat dissipation sensor response to various gases can be directly observed by considering the differential responses ΔR_c vs. percent composition shown in Fig. 2. As an illustrative example, a measured response of $\Delta R_c = +5.0 \Omega$ could be produced by either 16% Xe, 20% Kr, 49% CO₂, or 54% Ar in N₂; furthermore, any gas mixture with $k < k_{N_2}$ will have at least a partial overlap of response, over its full compositional range, with any of these mixture types. The response ambiguity is most striking when the experimental ΔR_c data averaged over the eight cantilever channels are displayed in a one-dimensional plot (Fig. 3), such that the overlap of the mixture data can be clearly observed. Since thermal conductivity, which underlies the heat dissipation mechanism, is not a unique characteristic of gases, sensor operations which rely solely on this detection approach must be limited to known, specific

scenarios – for example, detecting natural gas leaks in an indoor location where no other gas is expected to be present. If an unexpected gas were present, it might lead to false positives, or potentially mask the presence of the expected gas. For example, a mixture of CO₂ and CH₄ in the proper proportions may lead to a signal indistinguishable from the N₂ baseline reference.

An additional gas detection method that exploits the cantilever platform but generates sufficiently orthogonal response data would provide a convenient way to resolve the response ambiguity of a stand-alone thermal sensor. One such method involves measuring the subtle alteration of cantilever resonant frequency that occurs upon exposure to gases with different viscosities and densities. This method would also suffer from a response ambiguity similar to the thermal case, since these physical properties are also not unique amongst possible gas analytes. However, by utilizing the two sensing modalities in combination, and exploiting their mutual orthogonality through data reduction techniques such as principal components analysis (PCA) [29], a gas sensor with increased discrimination is obtained. The viscous damping of a resonating cantilever has been previously demonstrated as a viable means of identifying gases [30]. In this study, Xu et al. detected He, CH₄, N₂, Ar, and CO₂ by measuring shifts in the fundamental frequency with a resolution down to $\pm 0.05\%$. This resonant method of gas detection relies on a physical principle distinct from the heat dissipation method described in the previous section. Therefore, we expect that the data corresponding to each cantilever-based sensing approach for exposure to the same gases will exhibit at least some degree of mutual orthogonality. Using an expression for shifts of the vacuum fundamental frequency f_0 in the viscous damping regime [31]:

$$\frac{\Delta f_0}{f_0} = \frac{\pi \lambda^3}{3m_c} \left(\rho + \frac{9}{2\lambda} \sqrt{\frac{\mu}{\rho \pi f_0}} \right) \quad (1)$$

we simulated a data set for the eight binary mixtures types previously measured by the heat dissipation method. The continuum fluid assumption of the viscous damping regime is appropriate in these cases, since the heat dissipation data were obtained for gases at ambient atmospheric pressure. The density ρ and viscosity μ of each gas mixture were computed using the formulae described in our previous work [24]. The cantilever mass m_c was estimated at 9×10^{-12} kg based on the description provided in Ref. [24], and the nominal value of f_0 is measured at ~ 42 kHz. Previous theoretical treatments used contiguous spheres of radius λ in a “string of pearls” arrangement to model a viscously damped resonator [31, 32]; for the rectangular cantilevers used in this work, a value of $\lambda = 13$ μm was obtained by scaling the experimentally fitted results of Ref. [31] for a cantilever of the same proportional dimensions. A plot of relative frequency shifts vs. percent composition for the eight analyte mixtures is shown in Fig. 4. Since N_2 serves as a reference baseline in this study, and Eq. 1 represents frequency shifts with respect to the vacuum condition, relative shifts for each gas analyte were obtained by subtracting the value $\Delta f_0/f_0 = 1.30 \times 10^{-3}$ corresponding to an N_2 background at 760 Torr and 298 K.

The experimental ΔR_c data can be combined with the theoretical relative $\Delta f_0/f_0$ data to represent the response of a hypothetical dual-modality cantilever sensor. When PCA was applied to this combined data and the two leading components were plotted, vastly improved gas discrimination was observed (Fig. 5). Although some ambiguity remains – for example, He/N_2 and H_2/N_2 are still indistinguishable over most of their compositional range – the improvement over the stand-alone thermal sensor is considerable, as exemplified by the clear distinction between CH_4 and H_2 , which previously overlapped completely (cf. Fig. 3). Therefore, the

combined multimodality data yield more distinct analyte signatures that cannot be obtained from the detection modes individually.

The notion of increasing discrimination using MEMS-based multimodal approaches can be extended beyond cantilever transducers to an arbitrary number of sensing modes. The integration of multiple transducers and their supporting electronics, using current microfabrication and complementary metal-oxide-semiconductor (CMOS) processes, has been demonstrated by Hierlemann and co-workers [22, 33]. These authors have developed single-chip sensors combining polymer-functionalized cantilevers, capacitors, and calorimeters for chemical vapor detection [22], as well as metal oxide conductometric arrays for gas sensing [33]. Although we only demonstrate the gas selectivity of the dual-modality cantilever sensor in principle, the single-chip integration of the calorimetric and resonant modes would be straightforward using commercially proven technologies (e.g., the ZnO resonators on Veeco Active Probe cantilevers [34]).

5. Conclusions

We have presented a new method for detecting gases that combines two distinct physical mechanisms within a single piezoresistive microcantilever: heat dissipation and resonant damping in the viscous regime. An analysis of experimental data indicates that the sensor response is consistent with a heat dissipation mechanism dominated by the thermal conductivity of the gaseous analyte. Since this property is not unique amongst possible gas analytes, the resulting sensor responses have an inherent ambiguity, and cannot provide uniquely identifying signatures except in limited applications. Resonant damping in the viscous regime provides an additional gas detection modality that can be readily incorporated into the pre-existing cantilever

platform. By computing the theoretical shifts in cantilever resonant frequency resulting from viscous gas damping, and combining this simulated data with the experimental heat dissipation data using PCA, we have shown that a hypothetical dual-modality cantilever sensor can achieve improved gas discrimination compared to the modalities operating separately.

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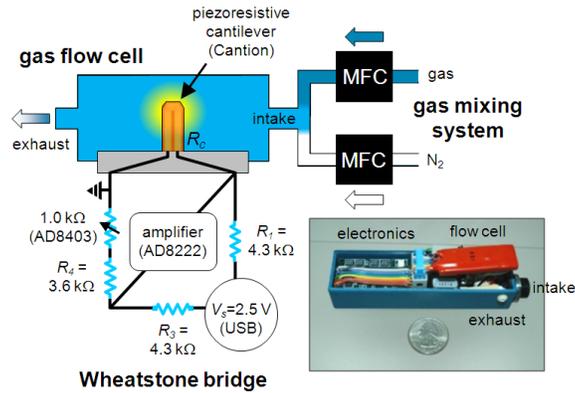


Fig. 1. Schematic overview of the experimental apparatus, including the gas sensor (Wheatstone circuit, gas flow cell) and gas mixing system; only one of the eight cantilevers and corresponding bridge circuits is represented for clarity. Inset: Photograph of the gas sensor next to a US quarter.

Table 1
Thermal conductivity k of various gases at 298 K (mW/m·K)
(adapted from Ref. [35]).

Gas	k
Xe	5.65
Kr	9.43
CO_2	16.9
Ar	17.7
N_2	25.8
CH_4	33.6
Ne	49.1
He	151.3
H_2	180.5

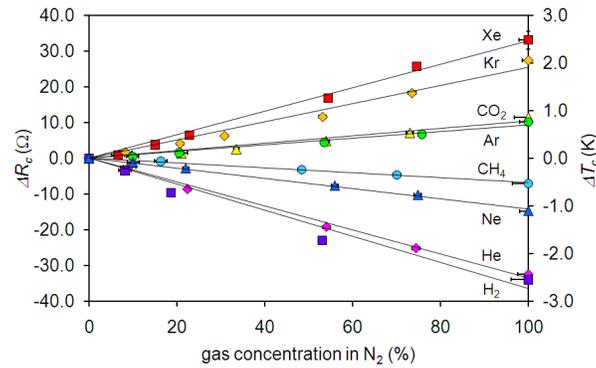


Fig. 2. Experimental plot of piezoresistor resistance change ΔR_c (*left axis*) and temperature change ΔT_c (*right axis*) vs. gas percent concentration in N_2 . Least squares regression lines are shown for each binary mixture data set, which represent the average responses of the eight cantilever channels. Error bars for each mixture data point: horizontal, from dosing uncertainty ($\sim 5\%$ of value); vertical, standard deviation ($\sim 2\%$ of value).

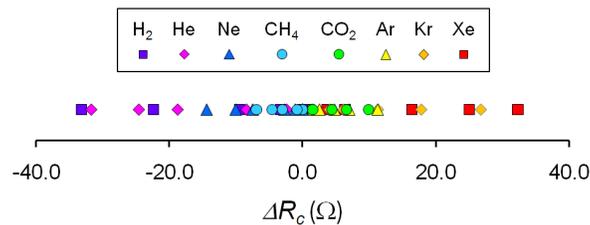


Fig. 3. One-dimensional plot of the experimental ΔR_c , averaged over the eight cantilever channels, for the eight binary mixtures examined in this work. The pure N_2 data point is located at $\Delta R_c = 0 \Omega$, with increasing gas concentration (up to 100%) for more the remote data points of each mixture type.

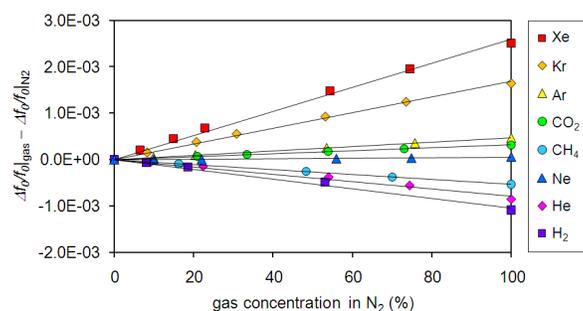


Fig. 4. Theoretical plot of relative $\Delta f_0/f_0$ vs. gas percent concentration in N_2 , with $\Delta f_0/f_0$ for pure N_2 at 760 Torr and 298 K as the reference value. Least squares regression lines are shown for each binary mixture data set.

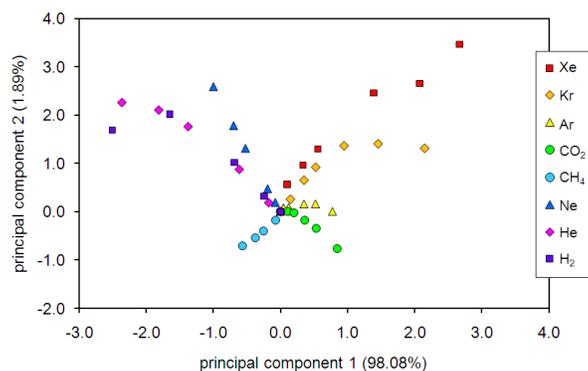


Fig. 5. Two-dimensional PCA plot of the experimental ΔR_c data combined with the theoretical relative $\Delta f_0/f_0$ data for the eight binary mixtures examined in this work (cf. Fig. 3). The pure N_2 data point is located at (0,0), with increasing gas concentration (up to 100%) for more the remote data points of each mixture type.